https://doi.org/10.48048/tis.2023.6809

Modification of Fresh-Water Clamshells (*Pilsbryoconcha exilis compressa*) as New Raw Material and its Application in the Biodiesel Production of Lard Oil

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Received: 1 March 2023, Revised: 22 March 2023, Accepted: 23 March 2023, Published: 31 March 2023

Abstract

In the present work, the catalytic activity and stability of the Fresh-water Clamshells-derived CaO catalyst were investigated by the transesterification reaction of lard oil. The physicochemical properties of lard oil as a raw material for biodiesel production compared with palm oil were also studied. The obtained CaO_FWC was characterized by various analytical techniques to evaluate the physicochemical properties consisting of TGA, SEM, XRD, XRF, BET surface area, FT-IR, Hammett indicator method, and CO_2-TPD. The results found that the fresh CaO_FWC showed the specific surface area, percentage of Ca element, total basic site, and basic strength of 8.293 m^2g^{-1}, 98.6 wt.%, 8.450 mmol g^{-1}, and $15 < H_ < 18.4$, respectively which similar to CaO commercial grade. In addition, the fresh CaO_FWC catalyst also presented high catalytic activity that gave %FAME of lard oil more than 96.5 %. However, the CaO_FWC catalyst could only reuse 3 times with the catalytic activity slightly decreased, and %FAME remained higher than 95 %. While the stability of the CaO_FWC catalyst was tested by storage for a long time to 180 days, this experimental data suggested that the CaO_FWC catalyst could preserve for only 30 days, with the catalytic efficiency remaining similar to the fresh CaO_FWC. Furthermore, the preservation and reusability of the catalyst were also studied in terms of the kinetic rate of reaction for use as a database to optimize the reaction conditions. Finally, the fuel properties of biodiesel products derived from lard oil and palm oil as raw materials and catalyzed by CaO_FWC catalyst met the specified standards both of EN-14214 and ASTM-D6751. Therefore, all the results of this work were excellent databases for utilizing and adding value to the Fresh-water Clamshells and lard oil as biomass sources for further development and development as renewable and alternative energy in Thailand.

Keywords: Biodiesel, Fresh-water Clamshells, CaO catalyst, Reaction kinetics, Transesterification reaction, Heterogeneous catalyst

Introduction

Biodiesel is a renewable and clean energy providently from vegetable oils or animal fats as a triglyceride and it is an alternative petroleum diesel engine, friendly environment, non-toxic, low-emission, and biodegradability. Moreover, the global concern of warming exhaust pollutants from the engine such as CO_2, SO_x, CO, NO_x, HC, and particulate matter (PM 2.5) as greenhouse caused combustion diesel fuel. Therefore, biodiesel oil is one of the best ways to substitute petroleum diesel oil because they have similar properties to petroleum diesel oil and can also decrease the amount of pollutant since the chemical structure of it is an organic compound and can be combusted cleanly [1-3]. Additionally, biodiesel oil is cheaper than petroleum diesel oil because it is produced from renewable sources such as palm oil, jatropha oil, soybean oil, castor oil, waste animal fat, and waste cooking oil through transesterification reaction [3-5].

The transesterification process is a reaction of triglyceride versus small molecule alcohol such as methanol or ethanol in the presence of a catalyst to convert the chemical structure of triglyceride, which was large molecule to mono alkyl ester (methyl ester or ethyl ester) as a small molecule [6,7]. Generally, the homogeneous base catalyst namely NaOH and KOH were used in the transesterification reaction to generate biodiesel products. However, these homogeneous catalysts can be reacted with free fatty acid (FFA) and moisture contents in the feedstock of oil to form soap products in the case of FFA and moisture higher than 0.5 and 0.1 wt.%, respectively. Moreover, removing these catalysts from biodiesel products is very difficult and requires large amounts of water to clean up the final biodiesel product. Hence, this process causes severe problems in the leading case environment and increases production costs [6-9]. To address this issue, developing solid base catalysts is an attractive choice for biodiesel production. The advantages of heterogeneous solid base catalysts are simple catalyst recovery and reusability, non-corrosive, more environment-friendly, easy and convenient for the purification of biodiesel products, and less energy and water consumption requirement [9-11].

Alkaline-earth metal oxides are usually applied as a solid base catalyst for transesterification because they have high basicity and are suitable for biodiesel production. The order of solid heterogeneous catalysts activity such as alkaline-earth metal oxide activity is BaO > SrO > CaO > MgO, respectively [12,13]. Calcium oxide (CaO) is one of the heterogeneous catalysts and one of the most promising catalysts for biodiesel production with excellent catalytic performance. Furthermore, it is also less solubility in methanol, very cheap due to being easy to generate from natural material sources, low toxicity, and environmentally friendly [10,11,14]. Several types of calcium sources from a natural waste material were studied and reported by many researchers to synthesize CaO catalysts such as river snail shells [9,15], eggshells [14,16,17], waste obtuse horn shells [18], chicken manure [19], walnut shell [20,21] and lobster shells [22].

There are several reports of biodiesel production through transesterification reactions using CaO as a heterogeneous catalyst derived from the calcination of natural raw materials. Niju *et al.* [14], presented that calcination-hydration-dehydration of eggshells obtained the high catalytic performance of the CaO catalyst. This catalyst at 5 wt.%, 12:1 methanol to oil molar ratio, and reaction temperature of 65 °C could be provided a biodiesel product of 94.52 % within the reaction time of 1 h. Lee *et al.* [18], studied the use of obtuse waste horn shell-derived CaO catalyst for the transesterification of palm oil to biodiesel. They found that the palm oil conversion was 86.75 % to biodiesel product under the reaction conditions of 6 h, methanol to oil ratio of 12:1, and 5 wt.% of catalyst loading amount. Additionally, they have also investigated the catalyst reusability. The results showed that the catalyst could reuse up to 3 times with catalytic activity higher than 70 % of palm oil conversion after the third cycle. Risso *et al.* [23], utilized waste shells of eggshells, oyster shells, and clam shells for biodiesel production of soybean oil. The results found that treated raw material in the process of catalyst preparation showed catalytic activity higher than the untreated sample by 2.5 times. Borah *et al.* [24], reported that 1 wt.% of Zn doped on eggshells to generate CaO nano-catalysts exhibited excellent catalytic activity to give a maximum biodiesel product of 96.74 % under the reaction of 20:1 methanol to oil molar ratio, 5 wt.% catalyst loading, 65 °C of reaction temperature, and 4 h of reaction time. Rabie *et al.* [25], applied the diatomite supported by CaO/MgO nanocomposite as a heterogeneous catalyst for biodiesel production from waste cooking oil. They found that under the optimum condition, namely 120 min of reaction time, the temperature at 90 °C, 6 wt.% of the catalyst loading amount, and a 1:15 oil: Methanol ratio could be provided the maximum biodiesel yield of over 96 %.

From the data of the report, using waste and natural raw materials to synthesize CaO catalysts for biodiesel production decreases the production process cost and reduces the impact on the environment. The utilization of these materials catalysts is the main objective of this research work. Thus, this work focused on studying the catalytic performance of the CaO catalyst prepared from Fresh-water Clamshells (*Pilsbryoconcha exilis compressa*) and used lard oil as a raw material for biodiesel production compared

with palm oil. The main point of this work consisted of studying the effect of reusability and preservation of the CaO_FWC catalyst on the performance catalytic activity. The synthesized CaO catalyst was studied for physical and chemical properties using techniques such as Thermogravimetric analysis (TGA), Scanning electron micrograph (SEM), X-ray diffraction (XRD), X-ray fluorescence (XRF), Brunauer-Emmett-Teller (BET) surface area, Fourier transforms infrared (FT-IR), and Temperature-Programmed desorption (CO_2-TPD). Furthermore, the preservation and reusability of the catalyst were also studied in terms of the kinetic rate of reaction for carefully investigating the catalytic activity. Finally, the qualities of biodiesel products were tested by following European Standard methods (EN14214), American Society for Testing and Material (ASTM) methods, and biodiesel product specifications in Thailand.

Materials and methods

Materials and catalyst preparation

Lard oil and palm oil were used as starting raw materials without any purification and they were purchased from commercial sources in the local market of Sakon Nakhon province, Thailand. **Table 1** presented the physicochemical properties of lard oil as a raw material for biodiesel production in this study compared with palm oil. The methanol analytical grade and Hammett indicators including phenolphthalein (pKa = 9.3), thymolphthalein (pKa = 9.9), indigo carmine (pKa = 12.2), 2,4-dinitroaniline (pKa = 15) and 4-nitroaniline (pKa = 18.4) were obtained from Sigma-Aldrich and Fluka, Thailand. Fresh-water Clamshells were collected from the local market in Ubon Ratchathani province, Thailand. The impurity and contaminants were cleaned with distilled water several times and then air-dried at 100 °C for 6 h. The cleaned and dried Fresh-water Clamshells were crushed, sieved to small particles, and calcined in a furnace at 800 °C for 3 h followed by the TG/DTA analysis result as shown in **Figure 3(a)** following the method of Phewphong *et al.* [6], Roschat *et al.* [9], and Niju *et al.* [10,14] The powder resulting material obtained (denoted as CaO_FWC) was preserved within the glass bottle that was completely sealed. As a commercial grade, calcium oxide (denoted as CaO_com), calcium carbonate (denoted as $CaCO_3$_com), calcium hydroxide ($Ca(OH)_2$), and potassium hydroxide (KOH) were purchased from Acros Chemical Co. Ltd.

Catalyst characterization

The obtained CaO_FWC powder was characterized by XRD using a PHILIPS X´Pert-MDP X-ray diffractometer, XRF with a PHILIPS MagiX spectrophotometer, and FT-IR spectrometer with a Perkin-Elmer RXI spectrometer. The physical properties namely the surface area and morphology were determined by BET by using Bel-sorp-mini II (Bel-Japan) and SEM using a JEOL JSM 5410LV. While the basic site value as the chemical properties were evaluated using the Hammett indicators method and CO_2-TPD with Chemisorption Analyzer (Belcat B) and the use of CO_2 as an investigation molecule. TGA was carried out on a Rigaku TG-DTA 8120 thermal analyzer to test the thermal decomposition and determine the suitable temperature for calcinating Fresh-water Clamshells to produce a CaO_FWC catalyst. In this research, the process to characterize, analyze, and evaluate the physicochemical properties of the obtained CaO_FWC powder followed referring to the method from the reports of Roschat *et al.* [9,26], Risso *et al.* [12], Niju *et al.* [10,14], Lee *et al.* [18], and Borah *et al.* [24].

Transesterification of lard oil using a CaO derived from Fresh-water Clamshells

Catalytic performance testing of the CaO_FWC via transesterification reaction of lard oil was carried out with a 250 mL 3-neck round-bottom flask batch reactor equipped with a reflux condenser, thermometer sensor, and magnetic stirrer. The first step of the process, the mixed methanol against CaO_FWC catalyst following the reaction conditions consists of catalyst loading amount of 5.0 wt.% to oil weight, methanol to oil molar ratios of 12:1 mol, reaction temperatures of 65 ± 2 °C, and reaction time of 60 - 360 min, respectively. Afterward, the operational reactor carefully added an amount of heated lard oil or palm oil of 50 mL (65 ± 2 °C). The reaction mixture was carefully controlled at a particular magnetic stirring rate of 500 rpm. The sampling method was applied to observe the reaction progress. A solution of the reaction mixture was sampled proximately 0.5 mL, evaporated excess methanol by a hot oven, and centrifuged to separate the CaO_FWC catalyst, glycerol as a by-product, and biodiesel product before the process of analysis of biodiesel yield.

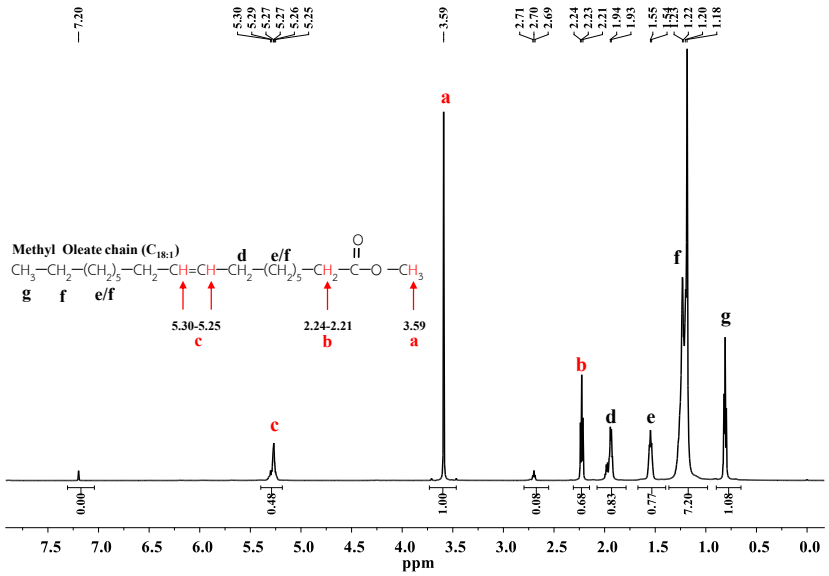

Figure 1 ^{1}H-NMR spectrum of the final biodiesel product obtained from lard oil and using a CaO_FWC as a catalyst.

The yield of biodiesel product was determined by nuclear magnetic resonance (^{1}H-NMR) technique on a Brüker AVANCE III HD (600 MHz) spectrometer in terms of the percentage of fatty acid methyl ester (%FAME) for the study of the kinetics rate reaction following the research reports of Roschat *et al.* [5,6,26] and Niju *et al.* [10,14]. The ^{1}H-NMR spectrum of the final biodiesel product obtained from lard oil and using a CaO_FWC as a catalyst was presented in **Figure 1**. A gas chromatograph analyzed the quality biodiesel product following the EN14214 standard method (GC-7890A) using a capillary column of DB-WAX with 30 m × 0.15 mm and a flame ionization detector according to the reports of Roschat *et al.* [5,6,26] and Cruz-Merida *et al.* [29]. **Figure 2** displayed a GC-chromatogram of the final biodiesel product obtained from lard oil using a CaO_FWC as a catalyst. For the reused experiment, the CaO_FWC solid catalyst was recovered by filtration for the next reactions, and all the reactions were run under the same conditions. Furthermore, the kinetics study of the transesterification reaction of lard oil catalyzed by the CaO_FWC catalyst was investigated via the reaction rate coefficient (k) value. The experimental method for the kinetics study in this work referred to the report of Roschat *et al.* [2,6,9], Krishnamurthy *et al.* [11], and Hebbar *et al.* [30]. Finally, the fuel properties of the obtained biodiesel were tested according to ASTM D6751 and EN 14214 standards method for bio-auto fuels [25-28].

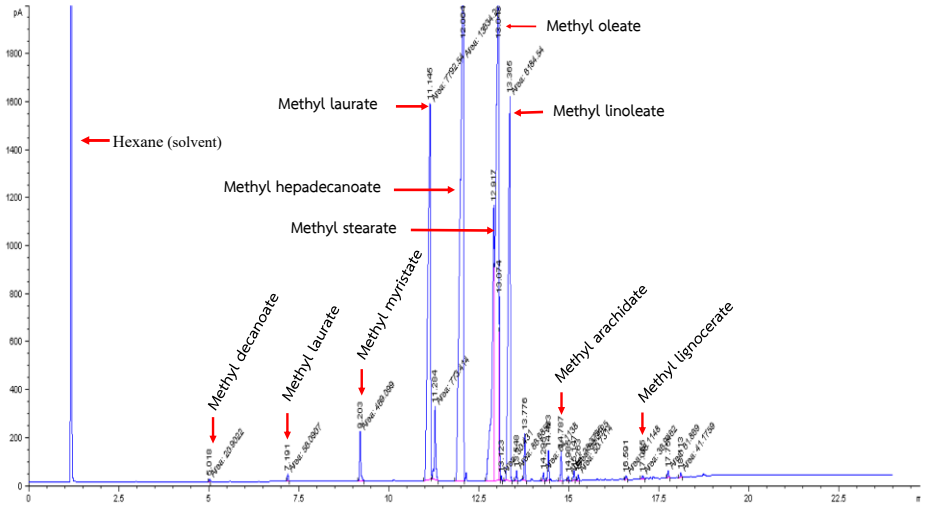

Figure 2 GC-chromatogram of the final biodiesel product obtained from lard oil using a CaO_FWC as a catalyst.

Table 1 Quality indices of lard oil as a raw material for biodiesel production in this study compared with palm olein oil.

Properties[a]	Lard oil	Palm oil
Kinematic viscosity @ 40 °C (cSt)	30.08	31.36
Density @15 °C (Kg m^{-3})	910.12	915.05
Acid number (mg KOH/g of oil)	1.94	0.31
FFAs content (wt.%)	0.98	0.16
Saponification value (mg KOH/g of oil)	192.44	196.38
Water content (%w/w oil)	0.51	0.67
Iodine value (g I_2/g of oil)	48.47	51.60
Fatty acid composition (%)		
- Decanoic acid ($C_{10:0}$)	0.13	-
- Lauric acid ($C_{12:0}$)	0.43	-
- Myristic acid ($C_{14:0}$)	1.92	0.11
- Palmitic acid ($C_{16:0}$)	23.53	36.73
- Palmitoleic acid ($C_{16:1}$)	2.55	3.33
- Stearic acid ($C_{18:0}$)	15.18	1.20
- Oleic acid ($C_{18:1}$)	41.84	46.07
- Linoleic acid ($C_{18:2}$)	12.67	12.03
- Linolenic acid ($C_{18:3}$)	1.09	0.38
- Arachidic acid ($C_{20:0}$)	0.66	0.15
Total saturated fatty acids composition (%)	41.85	38.19
Total unsaturated fatty acids composition (%)	58.15	61.81

Results and discussion

Physicochemical properties of lard oil as a raw material compared with palm oil

The physicochemical properties of lard oil as a raw material compared with palm oil were presented in **Table 1**. The obtained data found that lard oil and palm oil have similar properties except for acid number and free fatty acid. Lard oil has a higher acid number and free fatty acids than that palm oil due to the frying process of extracting the oil. Notwithstanding, both the acid number and free fatty acid of lard oil have a value that does not exceed the specified threshold of about 3 wt.% or 1.5 mg KOH/g of oil to affect transesterification reaction in biodiesel production. If the acid number and free fatty acid value were higher than the threshold, soap products would be produced instead of a saponification reaction [4,5,31]. Furthermore, the fatty acid composition of lard and palm oil was similar, especially oleic and palmitic acid, which were the major components. However, lard oil also consists of other fatty acid components, such as stearic acid and myristic acid, resulting in a higher total saturated fatty acids composition than palm oil. According to the results of the iodine value, the lard has a lower iodine value than that palm oil due to the presence of saturated hydrocarbons in the fatty acid molecular structure. The results of this study were consistent with the research report of Roschat *et al.* [26], and Ezekannagha *et al.* [32]. Accordingly, lard oil is another alternative raw material with suitable properties and potential for biodiesel production.

Catalyst characterization and catalytic tested

Fresh-water Clamshells powder was characterized by using X-ray diffraction (XRD), and the results of XRD patterns indicated that it was a $CaCO_3$ compound with a mixed orthorhombic and rhombohedral structure (**Figure 3(b)**). The resulting TG/DTA thermograms (**Figure 3(a)**) showed the phase decomposition of Fresh-water Clamshells powder sample in the range of 100 - 300 °C to be water and organic compound loose around 2.5 wt.%. In the range of 300 - 400 °C displayed $Ca(OH)_2$ phase

decomposition at approximately 2.5 wt.%. The significant decomposition occurred in the range of 650 - 800 °C which the $CaCO_3$ loose molecule of CO_2 to give the CaO phase about 53 wt.%. Thus, the temperature of 800 C was suitable for producing the CaO phase as an active material for transforming the lard oil into biodiesel oil. These results and discussion were also agreeable to the reports from Phewphong *et al.* [6], Krishnamurthy *et al.* [20], and Sani *et al.* [33], who have researched the synthesis of CaO material from natural shells. In addition, **Figure 3(b)** also illustrated XRD patterns of CaO_FWC derived from calcination of Fresh-water Clamshells material. The data revealed that the obtained CaO FWC matched the CaO phase and showed the structure as a simple cubic similar to CaO_com (PDF No. 00-048-1467).

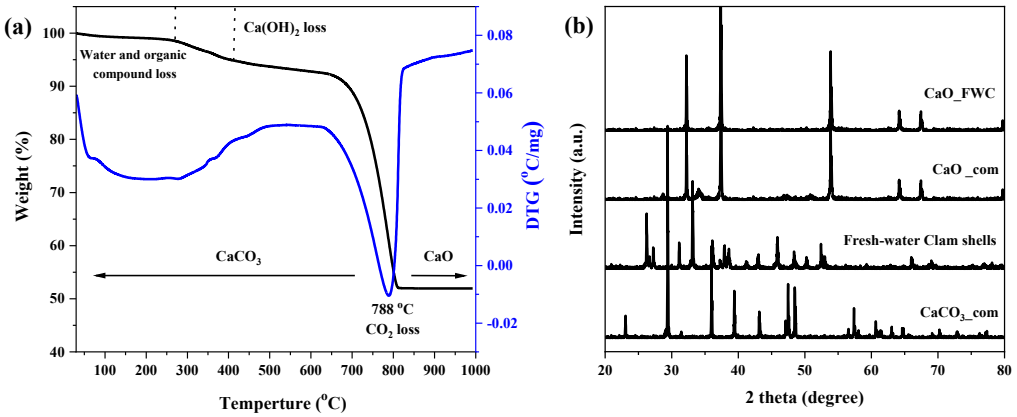

Figure 3 (a) TG/DTA thermograms of the Fresh-water Clamshells and (b) XRD patterns of CaO_FWC, CaO_com, Fresh-water Clamshells, and $CaCO_3$_com.

The percentage of Ca element investigated by X-ray fluorescence (XRF) technique indicated that CaO_FWC has an amount of Ca element composition over 98 wt.% and close with CaO_com as shown in **Table 2**. While the specific surface area, total basic site (CO_2-TPD desorption), and basic strength of the CaO_FWC catalysts showed a trend value higher than that of CaO_com. Corresponds to %FAME of lard oil which used the CaO_FWC as a catalyst has a higher yield than CaO_com at the same reaction conditions. The possible reasons for explaining the results of this experiment were the CaO_com adsorbed moisture in the air and became $Ca(OH)_2$ species [2,6,10]. The clear evidence showed that the $Ca(OH)_2$ minor phase revealed peaks mixed within the XRD patterns of CaO_com at 2θ degrees of 28.6, 34.1, 47.1 and 50.8 °, respectively. The morphology of the CaO FWC sample was proved by using the SEM technique and the SEM image depicted in **Figure 4(a)**. The apparent morphology was like a small sheet overlapping and agglomerated lumpenly. Moreover, it has a porosity distribution throughout the particle, and the particle size of the CaO FWC sample was about 5 - 30 µm.

Table 2 The specific surface area, percentage of Ca element, total basic site, basic strength of the CaO_FWC catalysts, and %FAME of lard oil using a CaO_FWC as a catalyst.

Catalyst	Specific surface area (m^2g^{-1})	Ca (wt.%)	Total basic site (mmol g^{-1})	basic strength (*H*)	%FAME of lard oil[c]
CaO_com	8.013	99.4	5.528	$15 < H\_ < 18.4$	96.83
CaO_FWC	8.293	98.6	8.450	$15 < H\_ < 18.4$	97.52
CaO_pre 180[a]	6.201	98.3	4.248	$12.2 < H\_ < 15$	64.49
CaO_deact[b]	3.329	98.3	1.883	$9.3 < H\_ < 12.2$	22.47

[a]CaO_pre 180 was denoted as the preserved CaO_FWC for 180 days.
[b]CaO_deact was denoted as the deactivated catalyst.
[c]The transesterification reaction conditions: Catalyst loading amount of 5 wt.%, methanol to oil molar ratio of 12:1, reaction temperature of 65 ± 2 °C, and reaction time of 180 min.

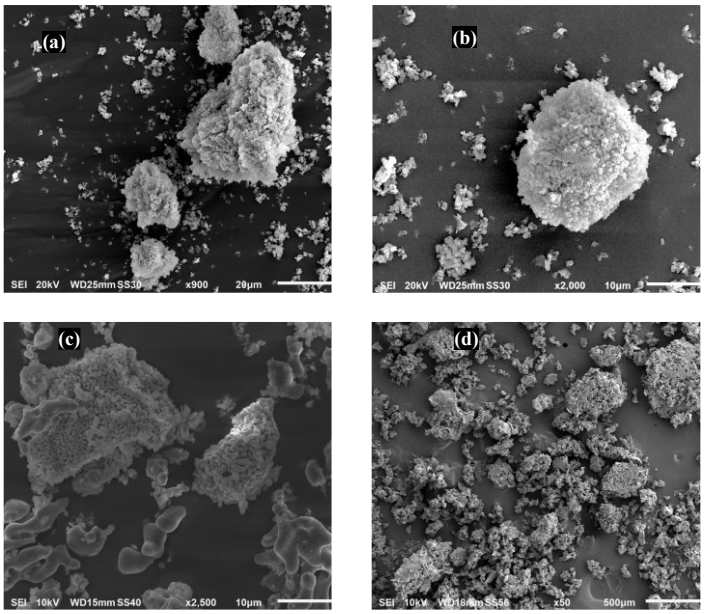

Figure 4 SEM image of (a) the fresh CaO_FWC, (b) the CaO_FWC catalyst after being preserved for 30 days, (c) the CaO_FWC catalyst after being preserved for 180 days, and (d) the deactivated CaO_FWC catalyst.

The effect reusability of the CaO_FWC catalyst on the catalytic activity

The effect reusability of the CaO_FWC catalyst on the %FAME of lard oil was revealed in **Figure 5(a)**. After each reaction, the CaO_FWC catalyst was filtered and washed with hexane and methanol to remove the reactant and product. Then it was reused without modification to run as a catalyst with the same condition. This study found that the CaO_FWC catalyst could be reused 3 times, and the catalytic activity was only slightly decreased. The biodiesel yield of lard oil was also higher than 95 %. However, the catalytic activity of the CaO_FWC catalyst drastically reduced after using it more than 3 times. At the reuse of the CaO_FWC catalyst 9 times, the resulting %FAME was reduced to about 20 %. The reasons explaining the deactivation of the catalyst were the active site of them damaged from the reaction mixture such as lard oil, biodiesel, and glycerol coverage over the surface area as demonstrated in **Figure 4(d)**. Agreement with the specific surface area, total basic site (CO_2-TPD desorption), and basic strength of the CaO_FWC catalysts were significantly decreased as shown in **Table 2**.

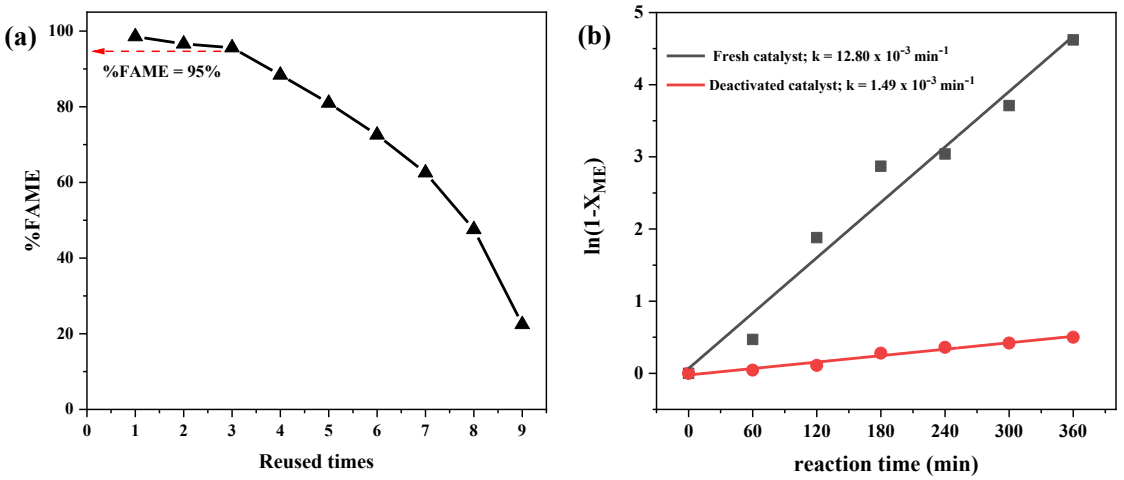

Figure 5 (a) the effects of reusability of the catalyst on the % and (b) comparison of the kinetics study on biodiesel production between using the fresh CaO_FWC and the deactivated CaO_FWC catalyst. The reaction conditions: Catalyst loading amount of 5 wt.%, methanol to oil molar ratio of 12:1, and reaction temperature of 65 ± 2 °C (the reaction time of 180 min for **Figure 5(a)**).

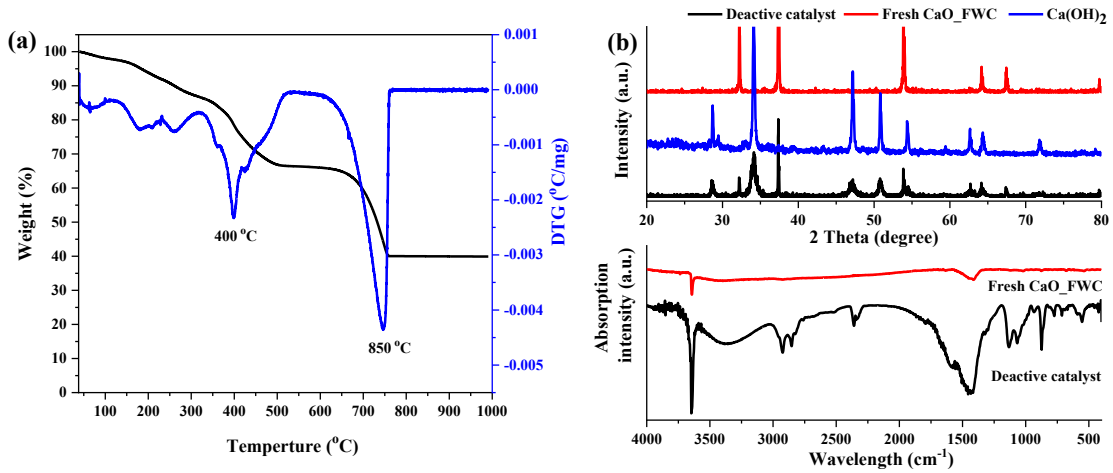

Figure 6 (a) TG/DTA thermograms of the deactivated CaO_FWC catalyst and (b) XRD patterns and FT-IR spectra of the CaO_FWC, $Ca(OH)_2$, and the deactivated CaO_FWC catalyst.

Moreover, TG/DTA thermograms, XRD patterns, and FT-IR spectra of the deactivated CaO_FWC catalyst were presented in **Figure 6**. TG/DTA thermograms results indicated that the deactivated CaO_FWC catalyst transformed into a $Ca(OH)_2$ and $CaCO_3$ compound followed the phase decomposition in the range of 400 to 800 °C denoted $Ca(OH)_2$ and $CaCO_3$ decomposed. While the XRD pattern and FT-IR spectra of the deactivated CaO_FWC catalyst found the $Ca(OH)_2$ and $CaCO_3$ specie, when compared with the fresh CaO_FWC catalyst, showed only the CaO phase. To confirm this phenomenon, the comparison of the kinetics study on biodiesel production between using the fresh and the deactivated CaO_FWC catalyst was also displayed in **Figure 5(b)**. The rate constant (k) value of using fresh and the deactivated CaO_FWC catalyst were 12.80×10^{-3} and 1.49×10^{-3} min^{-1}, respectively. This information suggested that both the catalysts exhibited very different catalytic activity under the same reaction conditions. All these results were supported by the research report of Roschat *et al.* [34,35], Changmai *et al.* [36], and Mohamed *et al.* [37], who studied the reuse of catalysts in biodiesel production.

The effect of the preservation CaO_FWC catalyst on the catalytic activity

The preservation effect of the CaO_FWC catalyst on the catalytic activity of biodiesel production was one of the important factors because it involved the cost of the production process. Suppose the catalyst can be stored long without decreasing its catalytic activity. In that case, it means the mass synthesis of catalysts at a time that can reduce the cost of biodiesel production. In this study, the CaO_FWC catalyst was preserved in an amber glass bottle, sealed tightly, and kept at room temperature for 180 days (6 months). The changes in chemical properties and catalytic activity of the CaO_FWC catalyst were monitored by taking the samples to be tested for the specified periods at 0 (fresh CaO_FWC), 30, 60, 90, and 180 days, respectively. The XRD patterns of the fresh CaO_FWC catalyst (0 days) compared with the Ca_FWC catalyst after being preserved for 30, 60, 90, and 180 days were displayed in **Figure 7(a)**. This result indicated that the CaO_FWC catalyst reacted with moisture and CO_2 in the air to give $Ca(OH)_2$ and $CaCO_3$ species after being preserved for 30, 60, 90, and 180 days [35,37,38]. This result was also consistent with the results of the FT-IR analysis as displayed in **Figure 7(b)**, which could be observed in the strong peak of the O–H stretching of $Ca(OH)_2$ at ~3641 cm^{-1}, C=O and C–O stretching of $CaCO_3$ at ~1577-1293 and 878 cm^{-1}, respectively. Furthermore, both the XRD patterns and FT-IR spectra of the CaO_FWC catalyst after being preserved for 180 days, showed more clearly the phase of the $Ca(OH)_2$ and $CaCO_3$ compounds.

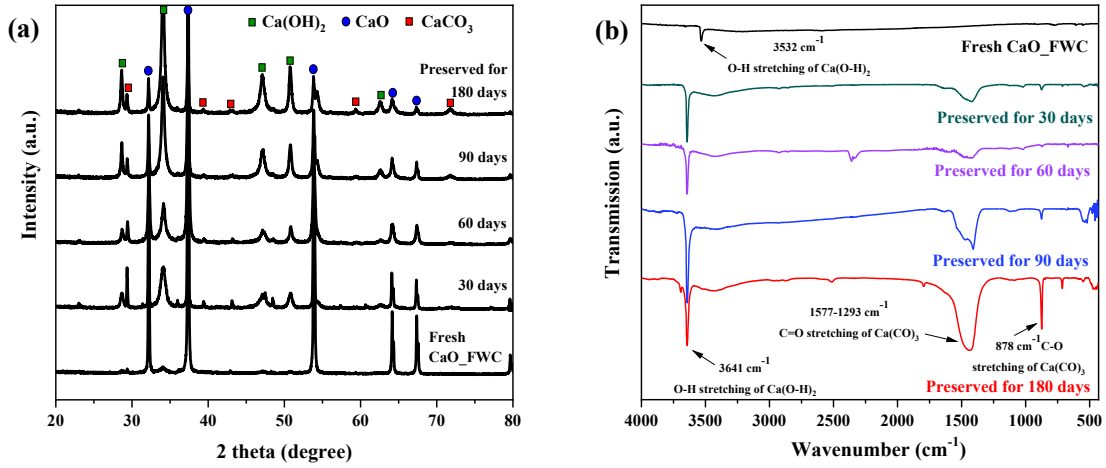

Figure 7 (a) XRD patterns and (b) FT-IR spectra of the fresh CaO_FWC (0 days) catalyst and CaO_FWC catalyst after being preserved for 30, 60, 90, and 180 days.

Additionally, the CO_2-TPD desorption curve of the fresh CaO_FWC (0 days), demonstrated in **Figure 8(a)**, also confirmed the result of the active site significantly decreasing after being preserved for 90 and 180 days. This data agreed with the basic strength ($H\_$) reduced to 12 .2< $H\_$< 15 of the maintained CaO_FWC for 180 days compared with the fresh CaO_FWC catalyst (0 days), as shown in **Table 2**. While the TG/DTA thermogram of the CaO_FWC catalyst after being preserved for 180 days, as depicted in **Figure 8(b)**, indicated that the significant mass loss was $Ca(OH)_2$ phase approximately 20 wt.%. In addition, the SEM image of the CaO_FWC catalyst after being preserved for 30 and 180 days was also presented in **Figures 4(b) - 4(c)**. The results indicated that the morphology of the CaO_FWC catalyst after being preserved for 30 days, slightly changed and remained intact. On the other hand, the CaO_FWC catalyst, after being stored for 180 days, markedly changed its morphology. **Figure 4(c)** showed that the morphology of the CaO_FWC catalyst was neatly together and agglomerated spheres more giant than the fresh CaO_FWC catalyst. This data accorded with the specific surface area of the preserved CaO_FWC for 180 days which significantly decreased from 8.293 m^2g^{-1} (the fresh CaO_FWC catalyst) to 6.201 m^2g^{-1}. The specific surface area of the preserved CaO_FWC for 180 days was reduced by 25.23 % compared to the fresh CaO_FWC catalyst.

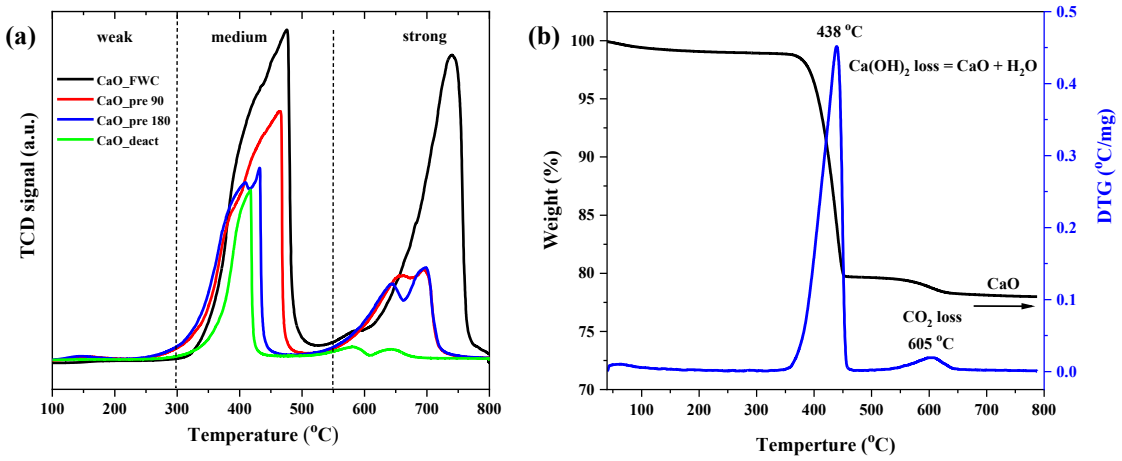

Figure 8 (a) CO_2-TPD desorption curve of the fresh CaO_FWC (0 days), CaO_FWC catalyst after being preserved for 90 and 180 days, and the deactivated CaO_FWC catalyst. (b) TG/DTA thermogram of the CaO_FWC catalyst after being preserved for 180 days.

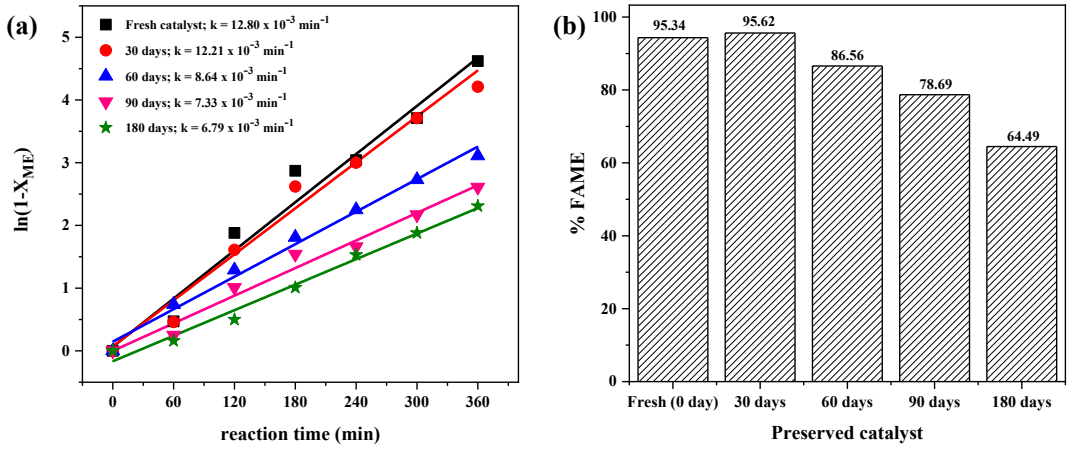

Figure 9 (a) comparison of the kinetics study and (b) the effects of catalytic activity on biodiesel production between using the fresh CaO_FWC (0 days) and the CaO_FWC catalyst after being preserved for 30, 60, 90, and 180 days. The reaction conditions: Catalyst loading amount of 5 wt.%, methanol to oil molar ratio of 12:1, and reaction temperature of 65 ± 2 °C (the reaction time of 180 min for **Figure 9(b)**).

Furthermore, the results displayed in **Figures 9(a) - 9(b)** also presented the comparison of the kinetics study and the effects of catalytic activity on biodiesel production between using the fresh CaO_FWC (0 days) and the CaO_FWC catalyst after being preserved for 30, 60, 90, and 180 days. The rate constant (k) value of the transesterification reaction with the used fresh CaO_FWC (0 days) was equal to 12.80×10^{-3} min^{-1}, higher than that of the preserved catalyst. In comparison, the k value of the used CaO_FWC catalyst after being kept for 30, 60, 90, and 180 days was 12.21×10^{-3}, 8.64×10^{-3}, 7.33×10^{-3} and 6.79×10^{-3} min^{-1}, respectively which has decreased significantly. This data has a similar trend with %FAME of the lard oil used in the same reaction conditions namely catalyst loading amount of 5 wt.%, methanol to oil molar ratio of 12:1, and reaction temperature of 65 ± 2 °C and the reaction time of 180 min. The results found that the fresh CaO_FWC (0 days) and CaO_FWC catalyst after being preserved for 30 days could be catalyzed to give %FAME higher than 95 %. In contrast, the experimental data also revealed that the CaO_FWC catalyst after being preserved for 60, 90, and 180 days had reduced catalytic efficiency with drastically decreased in the %FAME value. All these experimental data could be explained the decreased efficiency of the CaO_FWC catalyst after being preserved due to CaO as a major phase changing to $Ca(OH)_2$ and $CaCO_3$ phase. Several reports indicated that the CaO phase has a higher catalytic activity than $Ca(OH)_2$ and $CaCO_3$ phases because of the excellent properties of the total basic site and the basic strength of CaO meant the active site of the catalyst. These experimental results were consistent with the research report of Krishnamurthy *et al.* [11], Yaşar [16], Roschat *et al.* [35], Giammaria and Lefferts [39], Athar and Zaidi [40], Trisupakitti *et al.* [41]. Therefore, it could be concluded that the CaO catalyst derived from the Fresh-water Clamshells as a raw material could preserve for only 30 days (1 month), and the catalytic efficiency has also remained.

Fuel properties of biodiesel product catalyzed by using CaO_FWC catalyst

The fuel properties of biodiesel products derived from lard oil and compared with palm oil catalyzed by using CaO_FWC catalyst were presented in **Table 3**. The European standard test method (EN-14214) and the American Society for Testing and Material (ASTM-D6751) standard test method were applied to evaluate the physicochemical properties of the final biodiesel product following the reports of Roschat *et al.* [26,27], Cruz-Merida *et al.* [29], Paola *et al.* [42], Afzal *et al.* [43], Mohiddin *et al.* [44], and Taghipour *et al.* [45]. The yield of biodiesel products (% v/v) was calculated by the volume of the obtained biodiesel product divided by the volume of lard oil or palm oil as a starting material. The results found that the yield of lard oil biodiesel products was 88.54 %, while the yield of palm oil biodiesel products was 86.88 %. The percentage of fatty acid methyl ester content (%FAME) determined by GC and H-NMR technique has higher than 96.5 % for both lard oil and palm oil as raw material and catalyzed with CaO_FWC catalyst. This case indicated that lard oil and palm oil have a high potential for use as raw materials to produce biodiesel due to their lower acid value and free fatty acid.

In addition, the fuel properties of biodiesel products derived from lard oil and palm oil as raw materials and catalyzed by CaO_FWC catalyst met the specified standards both of EN-14214 and ASTM-D6751. In particular, the lard oil biodiesel product from this study showed physicochemical properties similar to the

research report of Roschat *et al.* [26] and Ezekannagha *et al.* [32], who studied the physicochemical properties of biodiesel products derived from lard oil and using eggshells as a green catalyst. Hence, all this study data indicated that lard oil as a raw material and Fresh-water Clamshells as a starting material to generate CaO_FWC catalyst for biodiesel production have great potential. Moreover, both raw materials were abundant biomass locally in Thailand and used relatively little. Therefore, all the results of this work were excellent databases for utilizing and adding value to biomass sources for further development and development as renewable and alternative energy.

Table 3 Fuel properties of biodiesel product derived from lard oil and palm oil as raw materials and catalyzed by CaO_FWC catalyst.

Fuel properties	Standard biodiesel	Lard oil biodiesel[c]	Palm oil biodiesel[c]
Yield of biodiesel product (% v/v)	-	88.54	86.88
Methyl ester content (%) by GC technique[a]	> 96.5	96.86	97.69
Methyl ester content by ^{1}H-NMR technique	-	97.35	98.12
Kinematic viscosity @ 40 °C (cSt)[a]	3.5 - 5.0	3.92	4.36
Density at 15 °C (kg/m^3)[a,b]	860 - 900	870	878
Acid number (mg KOH/g oil)[a,b]	< 0.5	0.30	0.30
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	0.024	0.036
Sulfated ash (%w/w of oil)[a,b]	≤ 0.02	0.011	0.015
Total contamination (ppm)[a]	< 24	12.6	19.3
Flash point (°C)[a]	> 120	182	188
Cloud point (°C)[b]	Report	+8	0
Pour point (°C)[b]	Report	+5	+8

[a]European standard (EN-14214) test method.
[b]American Society for Testing and Material (ASTM-D6751) standard test method.
[c]The reaction conditions: Catalyst loading amount of 5 wt.%, methanol to oil molar ratio of 12:1, reaction temperature of 65 ± 2 °C, and reaction time of 3 h.

Conclusions

This research work demonstrated the utilization of the Fresh-water Clamshells-derived CaO catalyst for producing biodiesel production from lard oil. The main point of this work consisted of studying the effect of reusability and preservation of the CaO_FWC catalyst on the performance of the catalytic activity and physicochemical properties, which were changed by this obtained catalyst. The results found that the properties of the CaO_FWC catalyst have a high performance equivalent to the CaO commercial grade under the same reaction conditions. The stability of the CaO_FWC catalyst was evaluated by reusing and preserving it for a long time to 180 days. The experimental data revealed that the reusability and preservation of the CaO_FWC catalyst were only able to reuse 3 times and kept for 30 days with the catalytic performance slightly decreased and %FAME was still more than 95 %. The reaction rate coefficient (k) value of the applied fresh and after being preserved for 30 days of CaO_FWC catalyst was 12.80×10^{-3} and 12.21×10^{-3} min^{-1}, respectively, whose values were not significantly different. The quality of biodiesel products derived from lard oil as a starting material and using CaO FWC as a catalyst met all the specified standards parameters of EN-14214 and ASTM-D6751 for biofuel products. Therefore, all the resulting data of this study suggested that using lard oil and the CaO_FWC catalyst for biodiesel production was another excellent option to utilize and add value to biomass materials in terms of the development of alternative and renewable energy in Thailand.

Acknowledgments

This project was supported by research funding from the National Research Council of Thailand (NRCT) (no. N42A650196) and Sakon Nakhon Rajabhat University, Thailand. The authors would like to gratefully thank the Biomass Energy Research Laboratory under the Center of Excellence on Alternative Energy, Sakon Nakhon Rajabhat University, and Ubon Ratchathani Rajabhat University, Thailand for supporting the apparatus and equipment. Additionally, the authors were also thankful to the National Energy Technology Center (ENTEC) for the analysis of the fuel properties of the final biodiesel oil product and the Vidyasirimedhi Institute of Science and Technology for the analysis of the sample by ^{1}H-NMR technique.

References

[1] AB Fadhil and AI Ahmed. Production of mixed methyl/ethyl esters from waste fish oil through transesterification with mixed methanol/ethanol system. *Chem. Eng. Comm.* 2018; **205**, 1157-66.

[2] W Roschat, P Butthichak, N Daengdet, S Phewphong, T Kaewpuang, P Moonsin, B Yoosuk and V Promarak. Kinetics stud of biodiesel production at room temperature based on eggshell-derived CaO as basic heterogeneous catalyst. *Eng. Appl. Sci. Res.* 2020; **47**, 361-73.

[3] K Suthar, A Dwivedi and M Joshipura. A review on separation and purification techniques for biodiesel production with special emphasis on Jatropha oil as a feedstock. *Asia Pac. J. Chem. Eng.* 2019; **14**, e2361.

[4] ST Keera, SM El Sabagh and AR Taman. Castor oil biodiesel production and optimization. *Egypt. J. Petrol.* 2018; **27**, 979-84.

[5] W Roschat, T Siritanon, B Yoosuk, T Sudyoadsuk and V Promarak. Rubber seed oil as potential non-edible feedstock for biodiesel production using heterogeneous catalyst in Thailand. *Renew. Energ.* 2017; **101**, 937-44.

[6] S Phewphong, W Roschat, P Pholsupho, P Moonsin, V Promarak and B Yoosuk. Biodiesel production process catalyzed by acid-treated golden apple snail shells (*Pomacea canaliculata*)-derived CaO as a high-performance and green catalyst. *Eng. Appl. Sci. Res.* 2022; **49**, 36-46.

[7] LI Saeed, AM Khalaf and AB Fadhil. Biodiesel production from milk thistle seed oil as nonedible oil by cosolvent esterification-transesterification process. *Asia Pac. J. Chem. Eng.* 2021; **16**, e2647.

[8] S Inthachai and W Roschat. The performance testing of biodiesel oil produced from waste cooking oil by using a prototype solar reactor for agricultural diesel engines. *J. Mater. Sci. Appl. Energ.* 2019; **8**, 398-407.

[9] W Roschat, T Siritanon, T Kaewpuang, B Yoosuk and V Promarak. Economical and green biodiesel production process using river snail shells-derived heterogeneous catalyst and co-solvent method. *Bioresource Tech.* 2016; **209**, 343-50.

[10] S Niju, S Meera, KM Begum and N Anantharaman. Enhancement of biodiesel synthesis over highly active CaO derived from natural white bivalve clam shell. *Arabian J. Chem.* 2016; **9**, 633-9.

[11] KN Krishnamurthy, SN Sridhara and CS Ananda Kumar. Optimization and kinetic study of biodiesel production from Hydnocarpus wightiana oil and dairy waste scum using snail shell CaO nano catalyst. *Renew. Energ.* 2020; **146**, 280-96.

[12] S Babak, H Iman and AS Abdullah. Alkaline earth metal oxide catalysts for biodiesel production from palm oil: Elucidation of process behaviors and modeling using response surface methodology. *Iranian J. Chem. Chem. Eng.* 2013; **32**, 113-26.

[13] S Maroa and F Inambao. A review of sustainable biodiesel production using biomass-derived heterogeneous catalysts. *Eng. Life Sci.* 2021; **21**, 790-824.

[14] S Niju, S Meera, KM Begum and N Anantharaman. Modification of egg shell and its application in biodiesel production. *J. Saudi Chem. Soc.* 2014; **18**, 702-6.

[15] S Kaewdaeng, P Sintuya and R Nirunsin. Biodiesel production using calcium oxide from river snail shell ash as catalyst. *Energ. Procedia* 2017; **138**, 937-42.

[16] F Yaşar. Biodiesel production via waste eggshell as a low-cost heterogeneous catalyst: Its effects on some critical fuel properties and comparison with CaO. *Fuel* 2019; **255**, 115828.

[17] YH Tan, MO Abdullah, CN Hipolito and YHT Yap. Waste ostrich and chicken eggshells as heterogeneous base catalyst for biodiesel production from used cooking oil: Catalyst characterization and biodiesel yield performance. *Appl. Energ.* 2015; **160**, 58-70.

[18] SL Lee, YC Wong, YP Tan and SY Yew. Transesterification of palm oil to biodiesel by using waste obtuse horn shell-derived CaO catalyst. *Energ. Convers. Manag.* 2015; **93**, 282-8.

[19] T Maneerung, S Kawi, Y Dai and CH Wang. Sustainable biodiesel production via transesterification of waste cooking oil by using CaO catalysts prepared from chicken manure. *Energ. Convers. Manag.* 2016; **123**, 487-97.
[20] MR Miladinovc, MV Zdujic, DN Veljovic, JB Krstic, IB Bankovic-Ilic, VB Veljkovic, OS Stamenkovic. Valorization of walnut shell ash as a catalyst for biodiesel production. *Renew. Energ.* 2020; **147**, 1033-43.
[21] A Alsultan, A Mijan and YH Taufiq-Yap. Preparation of activated carbon from walnut shell doped La and Ca catalyst for biodiesel production from waste cooking oil. *Mater. Sci. Forum* 2016; **840**, 348-52.
[22] Y Hangun-Balkir. Green biodiesel synthesis using waste shells as sustainable catalysts with Camelina sativa oil. *J. Chem.* 2016; **2016**, 6715232.
[23] R Risso, P Ferraz, S Meireles, I Fonseca and J Vital. Highly active Cao catalysts from waste shells of egg, oyster and clam for biodiesel production. *Appl. Catal. Gen.* 2018; **567**, 56-64.
[24] MJ Borah, A Das, V Das, N Bhuyan and D Deka. Transesterification of waste cooking oil for biodiesel production catalyzed by Zn substituted waste egg shell derived CaO nanocatalyst. *Fuel* 2019; **242**, 345-54.
[25] AM Rabie, M Shaban, MR Abukhadra, R Hosny, SA Ahmed and NA Negm. Diatomite supported by CaO/MgO nanocomposite as heterogeneous catalyst for biodiesel production from waste cooking oil. *J. Mol. Liq.* 2019; **279**, 224-31.
[26] W Roschat, S Phewphong, P Moonsin, P Pholsupho and S Yapan. Physicochemical properties of biodiesel product derived from lard oil using eggshells as a green catalyst. *Suranaree J. Sci. Tech.* 2020; **27**, 030025.
[27] W Roschat, S Phewphong, P Pholsupho, K Namwongsa, P Wongka, P Moonsin, B Yoosuk and V Promarak. The synthesis of a high-quality biodiesel product derived from Krabok (*Irvingia Malayana*) seed oil as a new raw material of Thailand. *Fuel* 2022; **308**, 122009.
[28] AB Fadhil. Production and characterization of liquid biofuels from locally available nonedible feedstocks. *Asia Pac. J. Chem. Eng.* 2021; **16**, 2572-91.
[29] J Cruz-Merida, G Corro, F Banuelos, D Montalvo and U Pal. Production of biodiesel from waste frying oil using waste calcareous-onyx as unique esterification and transesterification catalytic source. *Catal. Comm.* 2022; **172**, 106534.
[30] HRH Hebbar, MC Math and KV Yatish. Optimization and kinetic study of CaO nano-particles catalyzed biodiesel production from Bombax ceiba oil. *Energy* 2018; **143**, 25-34.
[31] K Kara, F Ouanji, EM Lotfi, ME Mahi, M Kacimi and M Ziyad. Biodiesel production from waste fish oil with high free fatty acid content from Moroccan fish-processing industries. *Egypt. J. Petrol.* 2018; **27**, 249-55.
[32] CB Ezekannagha, CN Ude and OD Onukwuli. Optimization of the methanolysis of lard oil in the production of biodiesel with response surface methodology. *Egypt. J. Petrol.* 2017; **26**, 1001-11.
[33] J1Sani, S Samir, II Rikoto, AD Tambuwal, A Sanda, SM Maishanu and MM Ladan. Production and characterization of heterogeneous catalyst (CaO) from snail shell for biodiesel production using waste cooking oil. *Innovat. Energ. Res.* 2017; **6**, 162.
[34] W Roschat, T Siritanon, B Yoosuk and V Promarak. Rice husk-derived sodium silicate as a highly efficient and low-cost basic heterogeneous catalyst for biodiesel production. *Energ. Convers. Manag.* 2016; **119**, 453-62.
[35] W Roschat, S Phewphong, A Thangthong, P Moonsind, B Yoosuk, T Kaewpuang and V Promarak. Catalytic performance enhancement of CaO by hydration-dehydration process for biodiesel production at room temperature. *Energ. Convers. Manag.* 2018; **165**, 1-7.
[36] B Changmai, C Vanlalveni, AP Ingle, R Bhagat and L Rokhum. Widely used catalysts in biodiesel production: A review. *RSC Adv.* 2020; **10**, 41625-79.
[37] RM Mohamed, GA Kadry, HA Abdel-Samad and ME Awad. High operative heterogeneous catalyst in biodiesel production from waste cooking oil. *Egypt. J. Petrol.* 2020; **29**, 59-65.
[38] K Vance, G Falzone, I Pignatelli, M Bauchy, M Balonis and G Sant. Direct carbonation of $Ca(OH)_2$ using liquid and supercritical CO_2: implications for carbon-neutral cementation. *Ind. Eng. Chem. Res.* 2015; **54**, 8908-18.
[39] G Giammaria and L Lefferts. Catalytic effect of water on calcium carbonate decomposition. *J. CO2 Utilization* 2019; **33**, 341-56.
[40] M Athar and S Zaidi. A review of the feedstocks, catalysts, and intensification techniques for sustainable biodiesel production. *J. Environ. Chem. Eng.* 2020; **8**, 104523.

[41] S Trisupakitti, C Ketwong, W Senajuk, C Phukapak and S Wiriyaumpaiwong. Golden apple cherry snail shell as catalyst for heterogeneous transesterification of biodiesel. *Braz. J. Chem. Eng.* 2018; **35**, 1283-91.
[42] MGD Paola, I Mazza, R Paletta, CG Lopresto and V Calabrò. Small-scale biodiesel production plants-an overview. *Energies* 2021; **14**, 1901.
[43] A Afzal, MEM Soudagar, A Belhocine, M Kareemullah, N Hossain, S Alshahrani, CA Saleel, R Subbiah, F Qureshi, MA Mujtaba. Thermal performance of compression ignition engine using high content biodiesels: A comparative study with diesel fuel. *Sustainability* 2021; **13**, 7688.
[44] MNB Mohiddin, YH Tan, YX Seow, J Kansedo, NM Mubarak, MO Abdullah, YS Chan, M Khalid. Evaluation on feedstock, technologies, catalyst and reactor for sustainable biodiesel production: A review. *J. Ind. Eng. Chem.* 2021; **98**, 60-81.
[45] A Taghipour, U Hornung, JA Ramirez, RJ Brown and TJ Rainey. Fractional distillation of algae based hydrothermal liquefaction biocrude for co-processing: Changes in the properties, storage stability, and miscibility with diesel. *Energ. Convers. Manag.* 2021; **236**, 114005.