

Kinetics study of biodiesel production at room temperature based on eggshell-derived CaO as basic heterogeneous catalyst

Wuttichai Roschat^{*1, 2)}, Piyamas Butthichak¹⁾, Natthasiya Daengdet¹⁾, Sunti Phewphong²⁾, Teadkai Kaewpuang³⁾, Preecha Moonsin⁴⁾, Boonyawan Yoosuk⁵⁾ and Vinich Promarak⁶⁾

¹⁾Program of Chemistry, Faculty of Science and Technology, Sakon Nakhon Rajabhat University, Sakon Nakhon 47000, Thailand

²⁾Biomass Energy Research Laboratory, Center of Excellence on Alternative Energy, Research and Development Institute, Sakon Nakhon Rajabhat University, Sakon Nakhon 47000, Thailand

³⁾Valaya Alongkorn Rajabhat University under the Royal Patronage, Sa Kaeo Center, Sa Kaeo 27000, Thailand

⁴⁾Program of Chemistry, Faculty of Science, Ubon Ratchathani Rajabhat University, Ubon Ratchathani 34000, Thailand

⁵⁾National Metal and Materials Technology Center (MTEC), Prathumthani 12120, Thailand

⁶⁾Department of Materials Science and Engineering, School of Molecular Science & Engineering, Vidyasirimedhi Institute of Science and Technology, Rayong 21210, Thailand

Received 8 January 2020

Revised 15 April 2020

Accepted 1 May 2020

Abstract

Eggshell-derived calcium oxide (CaO) materials were used as a heterogeneous base catalyst for biodiesel production from palm oil with methanol at room temperature ($30 \pm 2^\circ\text{C}$). The physicochemical properties of the catalyst were characterized by TG-DTA, XRD, FT-IR, SEM-EDX, Hammett indicator method, BET surface area, and CO_2 -TPD. The comparison of catalytic performance transesterification reaction at the temperature of 65°C against room temperature was investigated. Kinetics of the reaction were studied following pseudo-first order with under the optimal condition with catalyst loading amount of 15 wt.%, methanol to oil molar ratio of 15:1 and 10% v/v of the co-solvent in methanol. Under the optimal reaction conditions, the result showed that the yield of fatty acid methyl ester (FAME) was achieved 96.6% in 9 h and the obtained k value was $3.28 \times 10^{-1} \text{ h}^{-1}$ which higher than that of without co-solvent system ($3.07 \times 10^{-1} \text{ h}^{-1}$). After purification with a cation-exchange resin to remove calcium ion (Ca^{2+}), high-quality biodiesel product with the fuel properties of the biodiesel especially the major physicochemical properties meet both the ASTM and EN standard specifications. Utilization of waste eggshell-derived CaO as catalysts and performing the reaction at room temperature were not only environmentally-friendly technique but also decreasing biodiesel production cost.

Keywords: Kinetics study, Room temperature, Eggshell, Transesterification, Biodiesel product



Figure 1 The graphical abstract of this work.

*Corresponding author. Tel.: +664 297 0030

Email address: roschat1@gmail.com

doi: 10.14456/easr.2020.39

1. Introduction

Biodiesel is one of the most interesting renewable energy to substitute petroleum diesel due to its biodegradability, less emission greenhouse gases (HC, CO, CO₂, NO_x, SO_x), excellent lubricity and low toxicity [1-3]. Furthermore, biodiesel can be synthesized from vegetable oils (e.g. palm oil, rapeseed oil, jatropha oil, and rubber seed oil), waste cooking oil and animal fat (e.g. lard oil, chicken oil, and fish oil) as a triglyceride upon its reaction with a short-chain molecular alcohol such as methanol and ethanol in the presence of a catalyst throughout a transesterification or alcoholysis reaction [2, 4]. Typically, this reaction occurs at the reaction temperature around 60–70 °C to activate the substrates since the temperature affects the reaction kinetics [1, 5-6].

Generally, the transesterification reaction occurs via the homogeneous base catalysts namely NaOH and KOH. This common way can provide a high yield of biodiesel in short reaction time under mild reaction conditions [7-8]. Nevertheless, the major problem of this way is the cost to purify biodiesel products by washing with water to get rid of unreacted soluble catalyst and then the energy required to heat the product for water elimination. Hence, the use of homogeneous catalysts leads to a large amount of wastewater and energy consumption which directly increases the production cost [1, 4-5]. To solve these problems, the heterogeneous solid base catalysts have become the best choice for biodiesel production via transesterification reaction. The advantages of this catalyst consist of easily separated from the biodiesel product, less soluble and potentially reusable [2, 9-10]. Therefore, the amount of wastewater and energy consumption in the process can be decreased, thus, the cost production is alleviated.

Eggshell is one of the best raw materials for generating calcium oxide (CaO) as a heterogeneous solid base catalyst to be applied in the transesterification reaction. Many research articles have reported the utilization of eggshell derived CaO catalyst in biodiesel production because of its excellent and efficient catalytic properties, very cheap, environmentally friendly, less soluble in biodiesel product, easy to generate and non-toxic [1, 3, 11-13]. Viriya-empikul et al. [3, 12] found that the CaO obtained from calcination eggshell in air at 800 °C for 2–4 h showed high catalytic activity to produce biodiesel product over 90% of fatty acid methyl ester (FAME) in 2 h and higher than CaO derived from golden apple snail shell and meretrix venus shell under the optimum conditions of methanol to oil molar ratio of 12:1, catalyst loading amount of 10 wt.% and reaction temperature at 60 °C. Niju et al. [14] reported that CaO obtained from eggshell by the calcination–hydration–dehydration treatment exhibited higher catalytic activity than commercial CaO material. The results showed the methyl ester conversion of 67.57% for commercial CaO catalyst and 94.52% for CaO derived from eggshell under the similar conditions at a 5 wt.% catalyst (based on oil weight), methanol to oil ratio of 12:1, reaction temperature of 65 °C and reaction time of 1 h. Chavan et al. [15] presented the employing of CaO prepared from eggshell as a catalyst to synthesize biodiesel from jatropha oil. Following the optimum reaction conditions of methanol/oil molar ratio of 8:1, 2 wt.% of catalyst at 65±0.5 °C for 2.5 h, the yield of biodiesel product was 90%. Roschat et al. [16] reported the use of CaO catalyst derived from eggshell in the transesterification reaction of rubber seed oil as substrate successfully to obtain biodiesel product with the FAME yield

of 97% in 180 min under the conditions of catalyst content of 10 wt.%, methanol/oil molar ratio of 12:1 and reaction temperature of 60 °C. Thus, the use of eggshell derived CaO as a solid heterogeneous catalyst for biodiesel production in the industrial scale as possible.

Even though many researchers have reported the use of eggshell-derived CaO as a low-cost, high-efficiency and green basic heterogeneous catalyst for transesterification reaction to produce biodiesel product, most of the research has described that this reaction requires reaction temperature (60–65 °C) to activate the reaction mixture [11-16]. The energy consumption for the biodiesel production process is one of the major causes of high production cost [2]. Therefore, the present study focuses on using CaO obtained from the eggshell as a solid base heterogeneous catalyst and the applied technique of transesterification reaction at room temperature to synthesize biodiesel products. In addition, the novelty and emphasis of the present work also focus on the reaction kinetics of transesterification using CaO derived from eggshell both of the reaction at 65 °C and room temperature. The optimum conditions (the effect of catalyst loading amount, the effect of the methanol to oil molar ratio, and the effect of co-solvent) and reaction kinetics at room temperature were investigated. Finally, the physicochemical properties of the obtained purification and treatment biodiesel product were tested followed by the main fuel properties by using European Standard methods (EN14214) and American Society for Testing and Material (ASTM D6751) methods.

2. Materials and methods

2.1 Materials

Palm olein oil with the amount of free fatty acid of 0.31 mg KOH/g of oil and water content of 0.011% w/w, respectively, was obtained from commercial sources in the local market which was brand from Morakot Industries PCL., Thailand. Methanol, tetrahydrofuran (THF) and acetone analytical grade, hexane and acetone commercial-grade were purchased from Fluka. Calcium oxide (CaO), potassium hydroxide (KOH) and sodium hydroxide (NaOH) of analytical grade were obtained from Acros Chemical Co. Ltd. and Fluka. Phenolphthalein, thymolphthalein, indigo carmine, 2,4-dinitroaniline, and 4-nitroaniline applied as Hammett indicators in this work were purchased from Aldrich and Fluka.

2.2 Catalyst preparation and characterization

Eggshell as raw material for generating CaO catalyst in this present work was collected from local restaurant. It was washed with deionized water several times, dried in a hot air oven and then grinded by blender to get eggshell powder. The thermal gravimetric analysis (TGA) of eggshell by using a Rigaku TG/DTA 8120 thermal analyzer was employed to analyze the thermal decomposition and to determine the suitable temperature for calcination eggshell to produce CaO catalyst. Both the eggshell powder and resulting material after calcination eggshell powder were characterized by X-ray powder diffraction (XRD) using a Brüker D5005 X-ray diffractometer with Cu K α radiation ($k = 1.5418 \text{ \AA}$) at 1600 W, 40 kV, and 40 mA, and 0.02° per step. In addition, this work also used Fourier transform infrared (FT-IR) spectroscopy for characterization of the functional group of

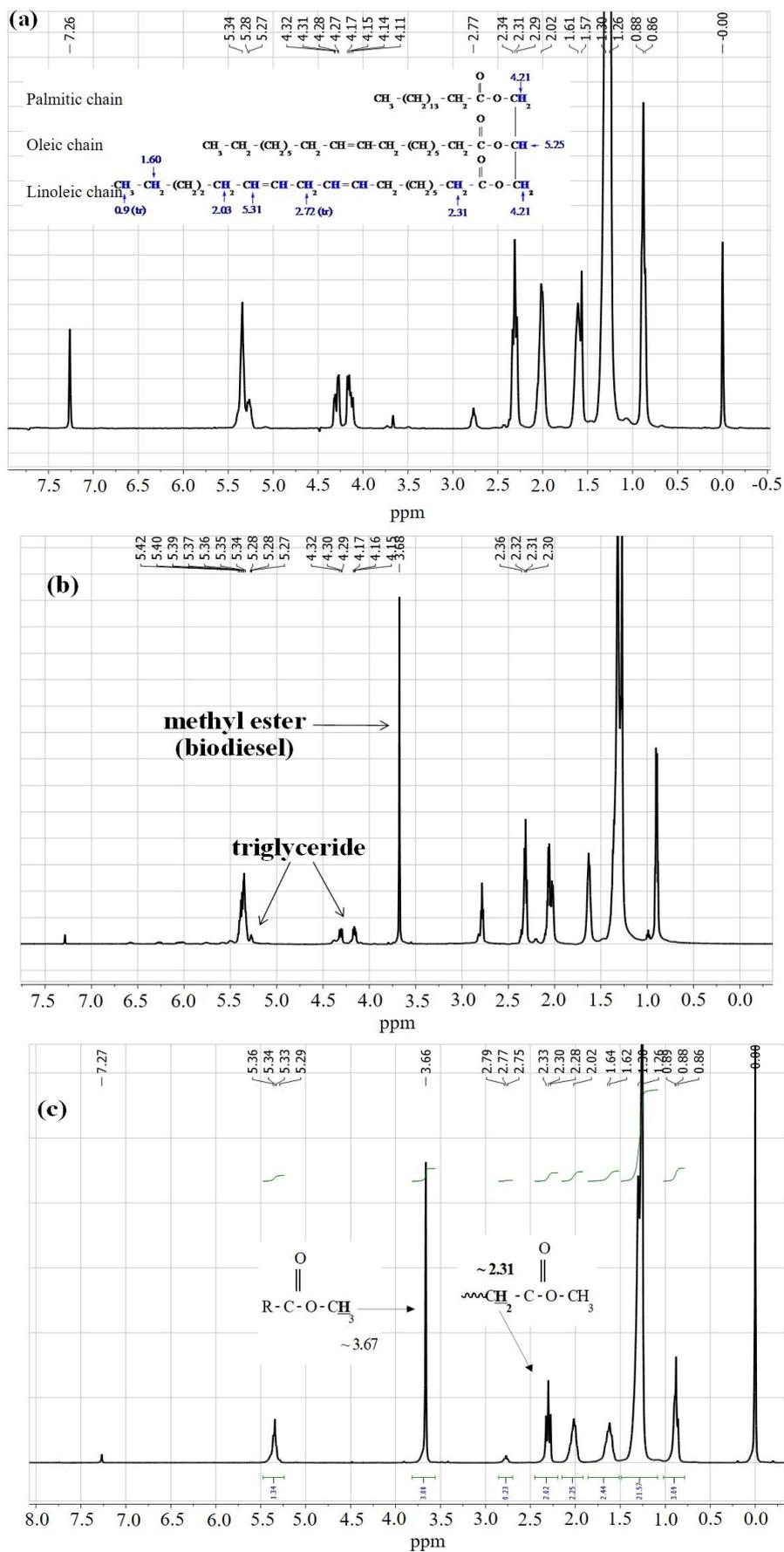


Figure 2 $^1\text{H-NMR}$ spectra of (a) palm olein oil as a starting material (triglyceride), (b) uncompleted transesterification (triglyceride + biodiesel) and (c) completed transesterification (biodiesel).

all material with Perkin–Elmer FT–IR spectroscopy spectrum RXI spectrometer.

The morphology of uncalcined eggshell compared with calcined eggshell was analyzed by scanning electron microscopy (SEM) with JEOL JSM 6010LV. The elemental chemical composition of eggshell was evaluated by Energy–Dispersive X–ray spectroscopy (EDX) with EDX–720 (Shimadzu, Japan). The surface area of calcined eggshell was determined by Brunauer–Emmett–Teller (BET) using a Bel–sorp–mini II (Bel–Japan) with adsorption and desorption isotherm at low temperature of N₂ gas and using He as a carrier gas. The basic strength (H_-) of all materials was evaluated by the Hammett indicator method. The temperature-programmed desorption method with CO₂ as an investigation molecule (CO₂–TPD) was applied to measure the total basic site property of calcined eggshell by using Chemisorption Analyzer of Belcat B and using He as a carrier gas.

2.3 Transesterification process using CaO derived from eggshell

A 250 mL three–neck round bottom flask equipped with condenser and thermometer was used as a batch reactor for transesterification reaction at room temperature (30±2 °C) of this study. Eggshell–derived CaO as a catalyst was mixed with methanol for 30 min and then added to palm oil. Experimental study on the reaction conditions was designed as follows: methanol to oil molar ratio of 12:1 to 21:1, catalyst loading amount of 5–20 wt.% corresponding to oil weight, amount of co–solvent (THF or acetone) to methanol of 10% (v/v) and fixed magnetic speed of 500 rpm. To monitor the reaction progress, 1 mL of the reaction mixture was sampled into a vial every 1 h for 12 h, centrifuged to separate the glycerol and catalyst, after that the excess methanol and co–solvent were eliminated by hot air oven. The obtained biodiesel product was evaluated in term of fatty acid methyl ester yield (%FAME) by the use of proton nuclear magnetic resonance spectroscopy (¹H–NMR) on a Brüker Ascend™ 600 MHz spectrometer and 0.03% v/v of tetramethylsilane (TMS) in CDCl₃ was used as an internal reference (0.00 ppm) and a solvent following the report of Roschat et al. [8, 16], Mathimani et al. [17] and Shimamoto

et al. [18]. The example of the ¹H–NMR spectra in this work was displayed in Figure 2 (a)–(c). A gas chromatograph on a GC–2010 Shimadzu was employed to determined %FAME of final biodiesel product according to EN 14214 standard methods referred to the report of Roschat et al. [5] and Mathimani et al. [17]. The example of the GC chromatogram of the final biodiesel product in this present work was illustrated in the Figure 3 following the method of Viriya–empikul et al. [3] and Roschat et al. [5]. Furthermore, the obtained biodiesel product was analyzed by FT–IR technique as shown in Figure 4 (a)–(c). The study of transesterification reaction kinetics in this work referred to the report of Roschat et al. [5], Muthukumar et al. [19], Hebbar et al. [20], Feyzi and Shahbazi [21].

3. Results and discussion

3.1 Catalyst characterization

The eggshell powder was characterized using XRD both before and after calcination and the result of XRD patterns was displayed in Figure 5(a). The XRD analysis indicated that eggshell powder used as a starting material to generate the catalyst was CaCO₃ compound (PDF No. 00–005–0586). This result conferred with the data from the EDX technique as specified that the major component of eggshell more than 99% was CaCO₃ as presented in Figure 6. To confirm the obtained result, TGA method was applied to analyze the decomposition of eggshell and the TG/DTA profile was shown in Figure 7. TG/DTA data showed the importance of decomposition of eggshell powder at 795 °C, whereas, CaCO₃ was changed to CaO phase. Hence, in this study, the calcination temperature at 800 °C for 3 h was selected to produce CaO catalyst from the eggshell.

After the calcination process of eggshell powder, the obtained material was characterized by XRD to prove the chemical composition. Figure 5(b) demonstrated XRD pattern of calcining eggshell which was consisted of CaO as the main phase (PDF No. 00–048–1467) and a minor phase included Ca(OH)₂ (PDF No. 00–044–1481) and CaCO₃ due to moisture and CO₂ in the air reacting with obtained CaO material. Additionally, the FT–IR technique was used to confirm the decomposition of eggshells to generate CaO

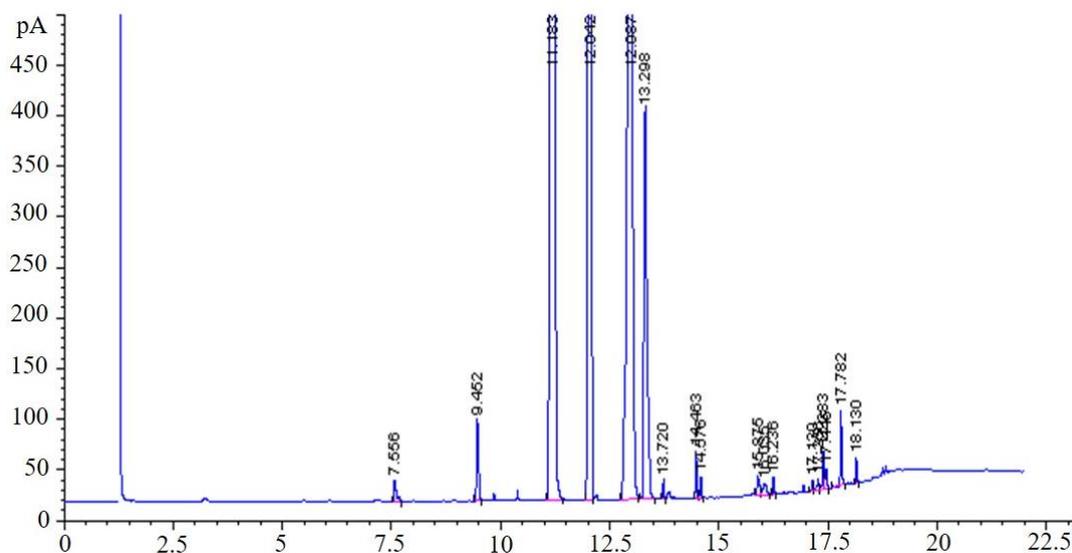


Figure 3 GC chromatogram of final biodiesel product

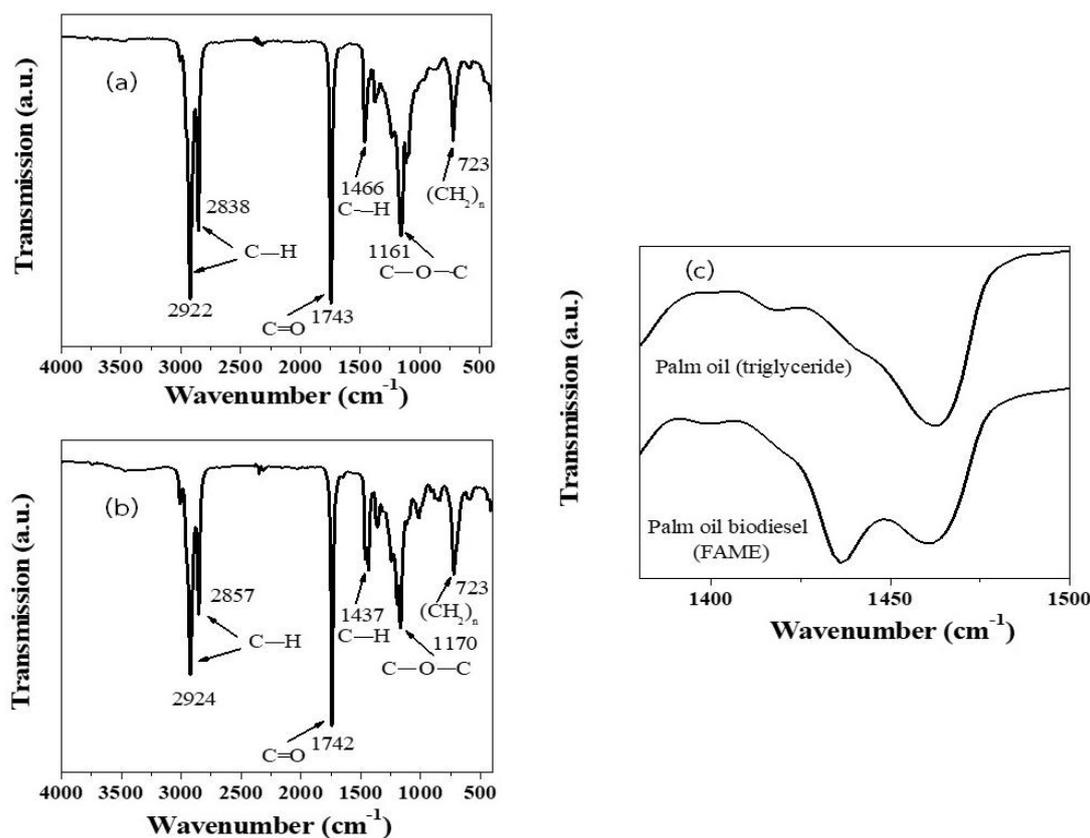


Figure 4 FT-IR spectrum of (a) palm oil (triglyceride), (b) biodiesel product and (c) an enlarged image in the range wave number of 1350-1500.

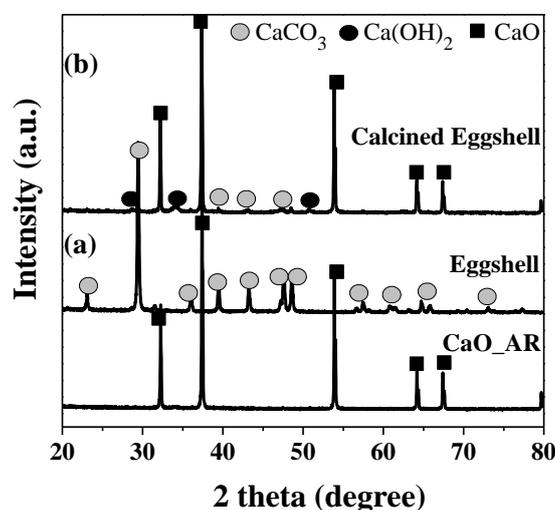


Figure 5 XRD patterns of (a) before calcination eggshell powder and (b) after calcination eggshell powder compared with CaO analytical grade (CaO_AR).

material. The results found that after calcining eggshell revealed only small peak hydroxyl group stretching around 3530–3545 cm^{-1} which was $\text{Ca}(\text{OH})_2$ phase (Figure 8). This result clearly confirms that eggshell was completely transformed to CaO with calcining at 800 °C for 3 h. The result and discussion agree with the report by Piker et al. [1], Viriya-empikul et al. [3] and Niju et al. [14] who have studied synthesis CaO from eggshell.

The morphology of eggshell powder compared with CaO material obtained from calcination eggshell powder at 800

°C for 3 h was investigated by SEM and the image illustrated in Figure 9. The SEM image of the eggshell (Figure 9(a)) was the rectangular shape and low porosity. After calcination of the eggshell (Figure 9(b)–(c)), the obtained CaO material displayed high porosity and high surface area. This phenomenon can be described that CaCO_3 compound of eggshell was transformed to be CaO by losing CO_2 gas which produced high porous on the surface. Consequently, this physical property was expected not only to leading a highly active site but also directly to result in high biodiesel yield.

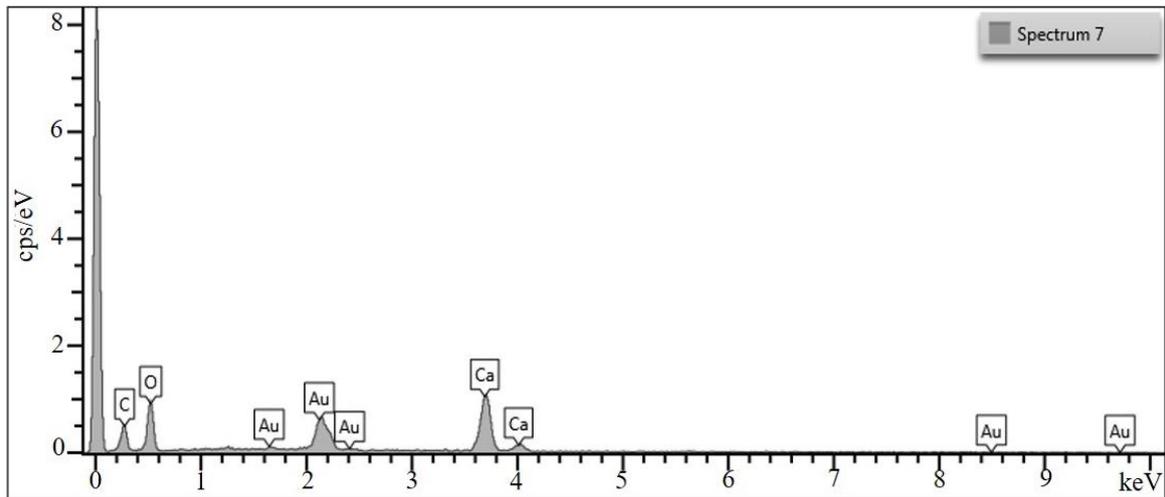


Figure 6 EDX spectrum of eggshell

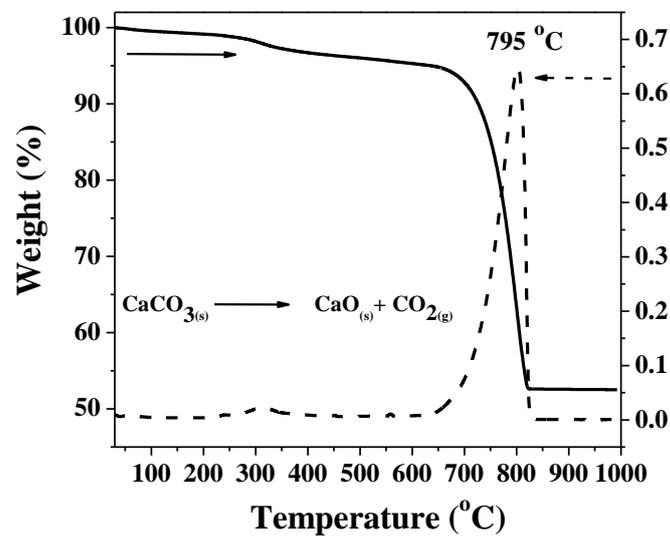


Figure 7 TG/DTA thermograms of eggshell

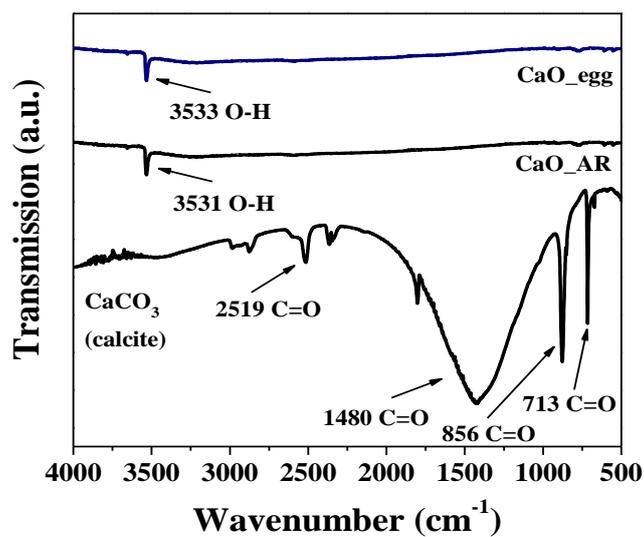


Figure 8 FT-IR spectra of the calcined eggshell at 800 °C for 3 h (CaO_egg) compared with CaO commercial grade (CaO_AR) and CaCO₃ (calcite)

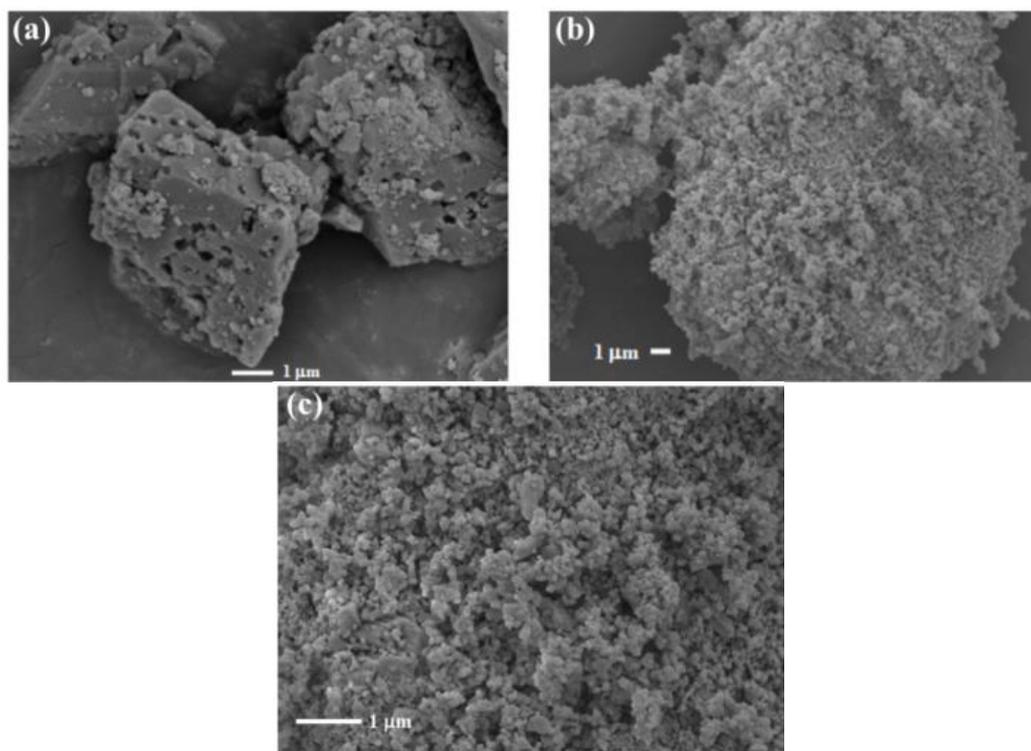


Figure 9 (a) SEM image of eggshell powder, (b) and (c) SEM image of CaO material obtained from calcination eggshell powder at 800 °C for 3 h.

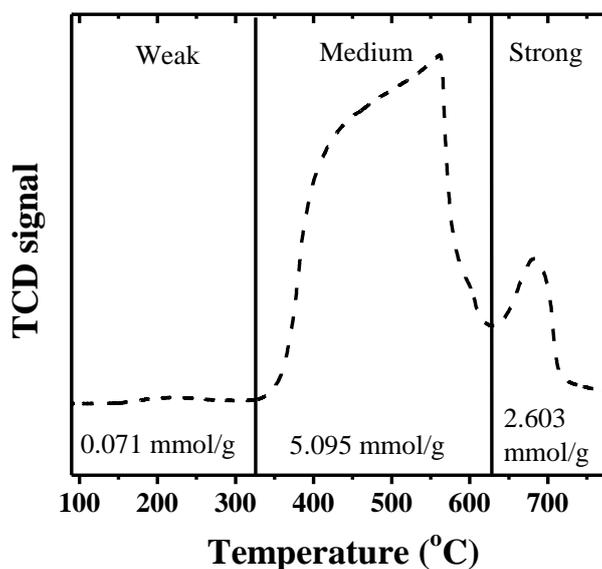


Figure 10 CO₂-TPD desorption curve of CaO catalyst obtained from calcination eggshell at 800 °C for 3 h.

The BET surface analysis was performed on eggshell-derived CaO catalyst due to the surface area of a solid catalyst directly impact on its active sites. The surface area of the obtained CaO material was found to be 2.8 m²g⁻¹ which higher than that of the report by Piker et al. [1] (1.8 m²g⁻¹), Viriya-empikul et al. [12] (1.1 m²g⁻¹) and Reddy et al. [22] (1 m²g⁻¹). The total pore volume and mean pore diameter of the sample were 7.011×10⁻³ cm³g⁻¹ and 10.243 nm, respectively. It is well known that the higher surface area of catalyst, the higher catalytic activity and it can be expected to lead to a higher yield of biodiesel product, respectively [1, 14, 23].

The CO₂-TPD was employed to prove the total basic site of the CaO catalyst and the result was illustrated in Figure 10. It can be seen that the CO₂-TPD curve of CaO catalyst obtained from calcination eggshell demonstrated a very small peak in the range of temperature from 100 to 330 °C which was specific as a weak basic site (0.071 mmol/g). On the other hand, the major peak of CO₂-TPD curve appeared between temperatures of 330 to 630 °C indicating a medium basic site (5.095 mmol/g). A strong basic site indicated at a temperature of 630 to 780 °C was found to be 2.603 mmol/g. Thus, the total basic site of CaO catalyst in this work was

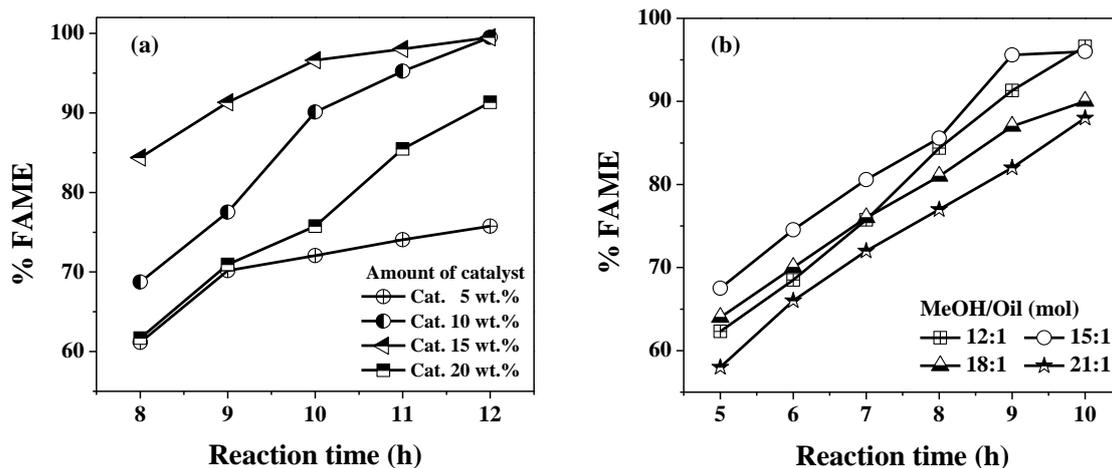


Figure 11 (a) the effects of catalyst concentration on %FAME yield room temperature ($30\pm 2^\circ\text{C}$) without co-solvent system (reaction conditions consist of methanol to oil molar ratio of 12:1 and amount of palm oil as 50 mL). (b) the yield of FAME at different methanol to oil molar ratios from 12:1 to 21:1 (reaction conditions consist of reaction temperature at room temperature ($30\pm 2^\circ\text{C}$), catalyst loading amount of 15 wt.%, without co-solvent system, and amount of palm oil as 50 mL).

7.796 mmol/g and the average basic site density calculated by total basic site divided BET surface area was to be 2.78 mmol/m². The basic strength (H_- value) of the obtained CaO catalyst was evaluated using a Hammett indicator method with observation a color of indicator change. This work found that the H_- value of the CaO catalyst was in the range of 15.0–18.4 because 2,4-dinitroaniline indicator ($pK_a = 15$) changed the color from yellow to purple, but 4-dinitroaniline indicator ($pK_a = 18.4$) did not change the color (yellow to orange). Therefore, all of the results of the catalyst characterization clearly indicated that the use of eggshells to derive CaO catalysts for biodiesel production was the high potential for expanding out of laboratory scale to the industrial scale.

3.2 Optimization of the reaction conditions for the synthesis of biodiesel product

3.2.1 The effect of CaO catalyst loading amount on the yield of biodiesel product

Since the focus of this work was to investigate the use of heterogeneous catalyst derived from calcination the eggshell to produce biodiesel product at room temperature, the influence of catalyst loading amount on the yield of the product was very important and interested. Several reports indicated that the surface area of the heterogeneous catalyst generated methoxide anion (CH_3O^-) from methanol which was a nucleophile molecule as a highly reactive species. Hence, an increasing amount of the catalyst directly effect promotes affects the formation of methoxide anion and greatly affects the biodiesel yield [2, 5, 24]. All of the experiments were, in this case, done following the same reaction condition of methanol to oil molar ratio of 12:1, reaction temperature of room temperature ($30\pm 2^\circ\text{C}$), without co-solvent system, amount of palm oil as 50 mL and the catalyst loading amount was varied in the range of 5–20 wt.%, respectively.

The results displayed that the trend of FAME yield was significantly increased as presented Figure 11(a) when the catalyst dosages was used from 5 wt.% to 15 wt.%. The yield of biodiesel gets a maximum at the condition of catalyst loading amount of 15 wt.% on the reaction time of 10 h.

Beyond 15 wt.% of the catalyst loading amount, FAME yield of biodiesel was dramatically decreased due to the effect of viscosity of reaction mixture was increased and directly affected to lower mass transfer of the reaction mixture. In addition, the decreasing of biodiesel yield may be caused by the reaction between triglyceride against catalyst to generate the soap products. These result agreed with the report of Feyzi et al., [21], Dai et al., [25], and Mahesh et al., [26].

3.2.2 The effect of the molar ratio of methanol to palm oil on FAME yield

Methanol to oil molar ratio not only directly affects the yield of biodiesel in terms of the shift of the equilibrium toward the direction of methyl ester formation but it is also one of the major factors affecting the production cost of biodiesel fuel [2, 5, 27]. If the reaction process of biodiesel production applied methanol less than the optimal requirement, the yield of biodiesel product may be obtained lower than that of the theoretical expectation. On the other hand, adding the excess methanol into the reaction system, the reaction required to shift the equilibrium reaction forward to enhance product brought about to inhibit of reaction by the hindrance from the dissolution of glycerol by-product in excessive methanol and this case led to increasing the overall cost of biodiesel product [27–28]. The result of the research found that methanol to oil molar ratio from 12:1 up to 15:1, %FAME yield and rate of reaction were increased and the reaction completed at 9 h in the case of using the molar ratio of 15:1 (Figure 11(b)). It is clear that 15:1 methanol to oil molar ratio was the optimal condition reaction. Beyond the molar ratio of 15:1, the yield of biodiesel has a tendency to decrease which corresponds to the reports of Takase et al. [27], Keera et al. [28], and Li et al. [29].

3.2.3 The effect of co-solvent on the yield of biodiesel product

In biodiesel production, the reaction system normally known that it consists of triglyceride as a starting material, alcohol (methanol or ethanol) as a reagent, and catalyst. In the part of the catalysts, they are separated into 2 types including homogeneous catalyst (e.g. NaOH, KOH, CH_3ONa , HCl, and H_2SO_4) and heterogeneous catalyst (e.g.

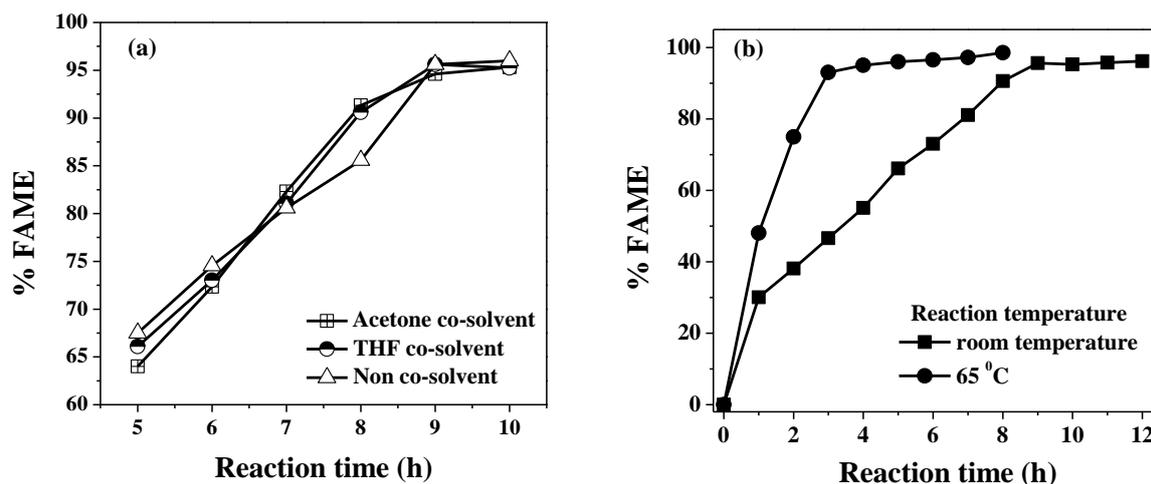


Figure 12 (a) the effect of co-solvent on the yield of FAME and (b) the comparison of biodiesel production at the reaction temperature of 65 °C with room temperature by the same reaction condition (reaction conditions; methanol to oil molar ratio of 15:1, catalyst loading amount of 15 wt.%, amount of palm oil loading of 50 mL; (a) reaction temperature at room temperature (30±2 °C), 10% v/v of co-solvent system; (b) amount of co-solvent (THF) to methanol of 10% v/v).

CaO, SrO, Zeolite Y, and Na/NaOH/ γ -Al₂O₃) [2, 5, 29-30]. In this work focus on the heterogeneous catalyst system, the reaction mixture included 3 phase namely catalyst as a solid phase, methanol as a hydrophilic phase, and palm oil as a hydrophobic phase. Therefore, the mixing of all 3 phases is very difficult and it was generally known to be the major problem to yield biodiesel product and rate of the reaction [31-33]. Consequently, the addition of co-solvent that can dissolve both methanol and palm oil is the methods to enhance the yield of biodiesel product and rate of the reaction.

As shown in Figure 12(a), the data demonstrated the efficiency of co-solvent on the yield of FAME. In this work, tetrahydrofuran (THF) and acetone were selected to be a co-solvent following the reports of Roschat et al. [8], Akkarawatkhosith et al. [32] and Mohammed-Dabo et al. [34] who have studied the use of many types of co-solvent and they found that both of THF and acetone were the best co-solvent to improve biodiesel production process. The results showed that adding 10% v/v of co-solvent compared to the ratio of methanol can promote the rate reaction to give the higher yield of biodiesel product while the reaction time can decrease. This data indicated that the reaction of biodiesel production completed at the reaction time of 9 h with the FAME yield over 96% both of with and without co-solvent.

Nevertheless, the kinetics study of biodiesel production at room temperature of both with and without co-solvent revealed that the rate constant (k) of the applied THF as a co-solvent was higher than that the case of acetone and without co-solvent system as depicted in Figure 13. This result can be ascribed that polarity and boiling point of THF were suitable to provide better homogeneity of the biodiesel reaction mixture than that of acetone. Notwithstanding, both of %FAME yield and k value of all the use of THF and acetone as a co-solvent were not difference. This data agreed with the report of Roschat et al. [8], Akkarawatkhosith et al. [32]. Accordingly, all of the results indicated that the optimal reaction condition of the biodiesel production process at room temperature was methanol to oil molar ratio of 15:1, catalyst loading amount of 15 wt.%, reaction temperature at room temperature (30±2 °C), amount of

co-solvent (THF or acetone) to methanol of 10% v/v, and amount of palm oil as 50 mL which can produce yield of FAME more than 96% at reaction time of 9 h.

As shown in Table 1, the data of the kinetics study of biodiesel production at room temperature catalyzed by eggshell-derived CaO as a catalyst can confirm the optimal reaction conditions by the k value which accorded against FAME yield at the time of 8 and 9 h. The results indicated that the reaction condition without a co-solvent system has a low k value while adding co-solvent in the reaction can improve the rate of the reaction. These results accorded to the report of Rosch et al. [8], Akkarawatkhosith et al. [32], and Mohammed-Dabo et al. [34] who presented adding a small amount of co-solvent in the reaction system which can enhance the kinetic rate of the reaction. However, the study also found that an increasing amount of co-solvent more than 10% v/v, the FAME yield showed decreasing in the trend of k value.

The excessive co-solvent loading amount may inhibit the transesterification reaction due to some molecule of the co-solvent may obstruct methanol molecule that reacted with triglyceride. In addition, it is possible that the overload of co-solvent might increase the polarity of the reaction system which had a great impact on the reaction mixture between palm oil with methanol. Moreover, the excessive co-solvent in the reaction also increases the viscosity of the reaction mixture which directly affected the dispersion of reactant and reagent into the catalyst. For these reasons, the addition of the co-solvent in a suitable quantity not only improves the kinetic rate reaction but also can reduce the reaction time and energy consumption.

3.3 Comparison of the rate reaction constant (k) of biodiesel production between the reactions at room temperature against at 65 °C

This study emphasized to compare the rate constant of the reaction performed at room temperature and at 65 °C under the optimal reaction condition. The result as displayed in Figure 14 found that the k value of the reaction temperature at 65 °C ($6.93 \times 10^{-1} \text{ h}^{-1}$) was higher than that of the reaction at the room temperature ($1.29 \times 10^{-1} \text{ h}^{-1}$)

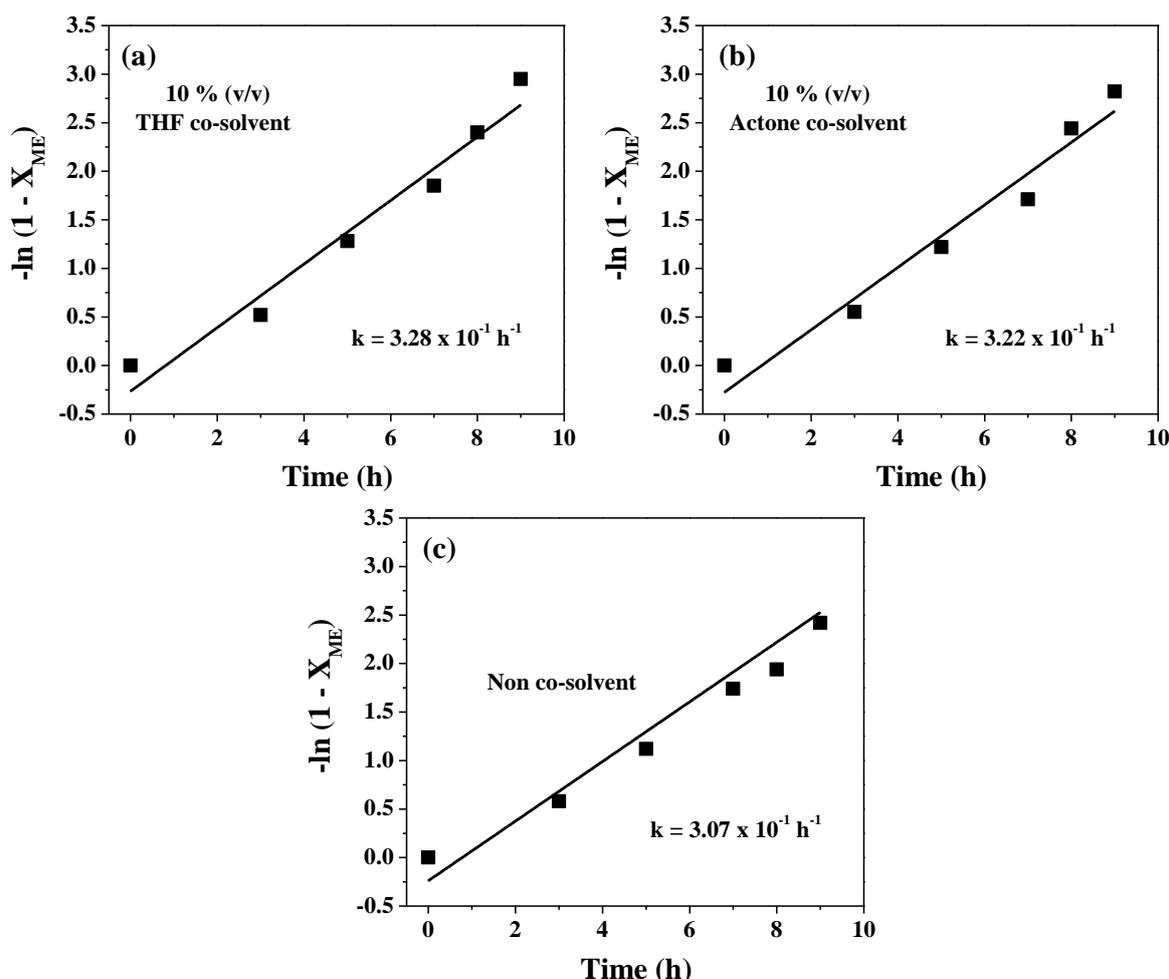


Figure 13 The kinetics study of biodiesel production at room temperature both with and without co-solvent system under the reaction conditions of methanol to oil molar ratio of 15:1, catalyst loading amount of 15 wt.%, reaction temperature at room temperature (30 ± 2 °C), and amount of palm oil as 50 mL.

Table 1 The kinetics study of biodiesel production at room temperature catalyzed by eggshell-derived CaO as a green catalyst.

Catalyst content wt.%	Transesterification parameters (reaction temperature at room temperature (30 ± 2 °C))			% FAME at reaction time	
	MeOH : oil molar ratio	Type of co-solvent (v/v)	k constant ($\times 10^{-1} \text{ h}^{-1}$)	8 h	9 h
5	12 : 1	non co-solvent	1.29	61.2	70.2
10	12 : 1	non co-solvent	2.56	68.7	77.5
15	12 : 1	non co-solvent	2.87	84.4	91.3
20	12 : 1	non co-solvent	2.66	61.7	70.9
15	15 : 1	non co-solvent	3.07	85.6	95.6
15	18 : 1	non co-solvent	2.92	81.0	87.2
15	21 : 1	non co-solvent	2.78	77.0	82.3
15	15 : 1	THF (10%)	3.28	90.6	96.6
15	15 : 1	THF (15%)	3.10	93.6	96.0
15	15 : 1	THF (20%)	2.73	88.3	90.1
15	15 : 1	Acetone (10%)	3.22	91.3	95.0
15	15 : 1	Acetone (15%)	3.02	93.3	92.8
15	15 : 1	Acetone (20%)	2.66	89.8	92.0

about 5.4 times. This data accorded that the reaction at the temperature of 65 °C completed within the reaction time of 3 h while the reaction at room temperature needs time around 9 h for completing as illustrated in Figure 12(b). In general, the reaction temperature extremely impacts the rate of

reaction because both the thermodynamics and kinetics of this reaction are very necessary to need the energy for transferring the reactant to the product [2, 26, 34-35]. The energy cost of biodiesel production is one of the most important factors which have to highly consider because it

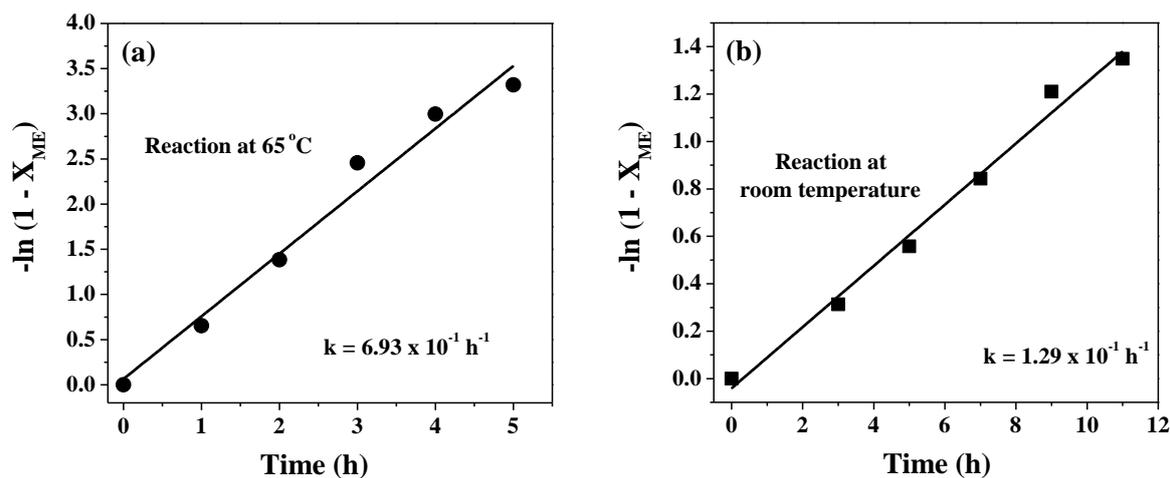


Figure 14 The comparison of the rate reaction constant (k) between the reactions performed at room temperature with at 65 °C under the optimal reaction condition of methanol to oil molar ratio of 15:1, catalyst loading amount of 15 wt.%, amount of co-solvent (THF) to methanol of 10% v/v, and amount of palm oil loading of 50 mL

Table 2 Physicochemical properties of biodiesel product

Properties	Unit	Standard Biodiesel	High-speed diesel	Palm oil	Palm oil biodiesel (this study)
Methyl ester content ^a	%	96.5	–	–	96.6
Kinematic Viscosity at 40 °C ^a	(cSt)	3.5 – 5	3.2	31.8	4.4
Density at 15 °C ^a	°C	860 – 900	839.7	901	874
Pour point ^b	°C	–15 to +16	–5	–	8
Cloud point ^b	°C	–3 to +12	5	–	0
Flash point ^a	°C	> 120	73	> 250	188
Oxidation Stability ^a	H	6	> 18	8.2	12.7
Copper strip corrosion ^{a,b}	Number	No. 1	No. 1	No. 1	No. 1
Water content ^a	%w/w oil	< 0.050	< 0.010	0.011	0.025
Total acid number ^{a,b}	mg KOH/g	< 0.5	< 0.02	0.28	0.22
Calcium ion content ^a	ppm	≤ 5	≤ 1	≤ 1	3.9
Total contamination ^a	ppm	≤ 24	12.5	870.8	18.2

^a European standard (EN – 14214)

^b American Society for Testing and Material (ASTM – D6751)

directly affected the price of biodiesel fuel. However, reducing energy consumption in the process of biodiesel production is one way to decrease the production cost which means to the cheaper biodiesel prices. Hence, the biodiesel production process in this study not only focuses on the use of CaO derived from eggshell as a low-cost green catalyst but also emphasize the reaction at room temperature to reduce the cost of energy consumption for utilizing in the industrial scale.

3.4 Physicochemical properties of the produced biodiesel

The fuel properties of the biodiesel product are very important for an application in the diesel engine. In this case, the major properties of biodiesel automotive fuels including density, kinematic viscosity, flash point, acid number, water content, copper strip corrosion, methyl ester content, oxidation stability, pour point, cloud point, calcium ion content and total contamination were selected to evaluate following the ASTM D-6751 and EN14214 standard methods as summarized in Table 2. This work separated the physicochemical properties of the biodiesel product into 3 groups consisting of the properties that involved the fuel

injection and ignition system in the engine (methyl ester content, kinematic viscosity, flash point, water content, and density), the oil properties that changed according to weather (pour point, cloud point, and oxidation stability) and the properties concerned with the corrosion and clogging in the engine (copper strip corrosion, total acid number, calcium ion content, and total contamination). The fuel injection and ignition system in the engine are some of the important factors of liquid fuel. Therefore, this is the main reason which vegetable oil or animal fat (biodiesel) was transformed into biodiesel oil (FAME) for reducing the viscosity [28]. In this case, the density and viscosity are likely in the same tendency and both properties depending on methyl ester content.

According to European standard (EN-14214) for biodiesel fuel, the methyl ester content must be at least 96.5%. The results found that biodiesel products produced at room temperature displayed FAME yield 96.6% which met within the standard criteria. In addition, the results also showed that both the density and viscosity of the obtained palm oil biodiesel decreased when compared with palm oil as raw material and within the accepted standard range. These data indicated that the obtained biodiesel oil can be

employed very well with the diesel engine as replacement petroleum diesel oil especially a single-cylinder diesel engine for agriculture. Additionally, the data in Table 2 revealed that the biodiesel oil produced from eggshell-derived CaO catalyst and reacted at room temperature has the fuel properties in the period of the range acceptable following the ASTM-D6751 and EN-14214 standards namely the copper strip corrosion, total acid number, calcium ion content, and total contamination. Thus, it can be concluded that the use of the biodiesel product does not cause the problem involving the corrosion and clogging that damaged the engine.

Finally, the factors of biodiesel fuel which are related to the physical and chemical change by environmental factors consisting of pour point, cloud point, and oxidation stability were accepted with the required standard of bio-auto fuels. These results suggest that the obtained biodiesel oil can tolerate the decreasing of the temperature and it would be in a liquid phase that could flow to the combustion chamber. Furthermore, the storage of the biodiesel product under the atmosphere is one of the critical factors that should be carefully considered, since biodiesel oil can react with moisture and oxidation with air to produce carboxylic acid. This case directly increases the total acid number of biodiesel oil. It is generally known that the standard of biodiesel fuel required oxidation stability at least 6 h. This result found that the oxidation stability of the final biodiesel product was higher than 12 h which was 2 times higher than that of the defined standard. Consequently, biodiesel oil produced at room temperature in this work shows the high-quality properties according to both the ASTM and EN standard specifications for biomass automotive fuel.

4. Conclusions

Eggshells-derived CaO was used as a green catalyst for biodiesel production from palm olein oil at room temperature. The optimal reaction conditions, in this work, were; catalyst loading amount of 15 wt.%, methanol to oil molar ratio of 15:1 and adding 10% v/v of the THF as a co-solvent in methanol which could provide biodiesel yield of 96.6% within 9 h. The kinetics study of biodiesel production at room temperature found that the k value of the reaction temperature at 65 °C was higher than that of the reaction at the room temperature around 5.4 times. The obtained biodiesel product from the reaction at room temperature has high-quality properties and within the required standards specifications for biodiesel fuel. Eggshell-derived CaO as a green catalyst, the performed reaction at room temperature, and adding the co-solvent are the way to produce biodiesel oil which can decrease efficiently the energy consumption and production cost.

5. Acknowledgements

The authors gratefully appreciated to Program of Chemistry, Faculty of Science and Technology and Biomass Energy Research Laboratory under Center of Excellence on Alternative Energy and Research and Development Institute, Sakon Nakhon Rajabhat University–Thailand, for supporting the equipment and tools. We would like to acknowledge Vidyasirimedhi Institute of Science and Technology–Thailand, for evaluation yield of biodiesel product by $^1\text{H-NMR}$ technique and National Metal and Materials Technology Center (MTEC)–Thailand, for

analysis of the fuel properties of the obtained biodiesel product.

6. References

- [1] Piker A, Tabah B, Perkas N, Gedanken A. A green and low-cost room temperature biodiesel production method from waste oil using egg shells as catalyst. *Fuel*. 2016;182:34-41.
- [2] Roschat W, Phewphong S, Thangthong A, Moonsin P, Yoosuk B, Kaewpuang P, et al. Catalytic performance enhancement of CaO by hydration-dehydration process for biodiesel production at room temperature. *Energy Convers Manage*. 2018;165:1-7.
- [3] Viriya-empikul N, Krasae P, Nualpaeng W, Yoosuk B, Faungnawakij K. Biodiesel production over Ca-based solid catalysts derived from industrial wastes. *Fuel*. 2012;92:239-44.
- [4] Syazwani ON, Teo SH, Islam A, Taufiq-Yap YH. Transesterification activity and characterization of natural CaO derived from waste venus clam (*Tapesbelcheri S.*) material for enhancement of biodiesel production. *Process Saf Environ*. 2017;105:303-15.
- [5] Roschat W, Siritanon T, Yoosuk B, Promarak V. Biodiesel production from palm oil using hydrated lime-derived CaO as a low-cost basic heterogeneous catalyst. *Energy Convers Manage*. 2016;108:459-67.
- [6] Yaakob Z, Mohammada M, Alherbawi M, Alam Z, Sopian K. Overview of the production of biodiesel from waste cooking oil. *Renew Sust Energ Rev*. 2013;18:184-93.
- [7] Lee SL, Wong YC, Tan YP, Yew SY. Transesterification of palm oil to biodiesel by using waste obtuse horn shell-derived CaO catalyst. *Energy Convers Manage*. 2015;93:282-8.
- [8] Roschat W, Siritanon T, Yoosuk B, Promarak V. Economical and green biodiesel production process using river snail shells-derived heterogeneous catalyst and co-solvent method. *Bioresour Technol*. 2016;209:343-50.
- [9] Maneerung T, Kawi S, Dai Y, Wang CH. Sustainable biodiesel production via transesterification of waste cooking oil by using CaO catalysts prepared from chicken manure. *Energy Convers Manage*. 2016;123:487-97.
- [10] Galadima A, Muraza O. Biodiesel production from algae by using heterogeneous catalysts: a critical review. *Energy*. 2014;78:72-83.
- [11] Wei Z, Xu C, Li B. Application of waste eggshell as low-cost solid catalyst for biodiesel production. *Bioresour Technol*. 2009;100:2883-5.
- [12] Viriya-empikul N, Krasae P, Puttasawat B, Yoosuk B, Chollacoop N, Faungnawakij K. Waste shells of mollusk and egg as biodiesel production catalysts. *Bioresour Technol*. 2010;101:3765-7.
- [13] Roschat W, Najai K, Kaewpuang T, Moonsin P. Biodiesel production via ethanolysis catalyzed by CaO derived from eggshell as low-cost basic heterogeneous catalyst. *J Mater Sci App Ener*. 2017;6(3):220-5.
- [14] Niju S, Meera S, Begum KM, Anantharaman N. Modification of egg shell and its application in biodiesel production. *J Saudi Chem Soc*. 2014;18:702-6.
- [15] Chavan SB, Kumbhar RR, Madhu D, Singh B, Sharma YC. Synthesis of biodiesel from *Jatropha curcas* oil

- using waste eggshell and study of its fuel properties. RSC Adv. 2015;5:63596-604.
- [16] Roschat W, Siritanon T, Yoosuk B, Sudyoadsuk T, Promarak V. Rubber seed oil as potential non-edible feedstock for biodiesel production using heterogeneous catalyst in Thailand. Renew Energ. 2017;101:937-44.
- [17] Mathimani T, Uma L, Prabakaran D. Homogeneous acid catalysed transesterification of marine microalga *Chlorella* sp. BDUG 91771 lipid-An efficient biodiesel yield and its characterization. Renew Energ. 2015;81:523-33.
- [18] Shimamoto GG, Bianchessi LF, Tubino M. Alternative method to quantify biodiesel and vegetable oil in dieselbiodiesel blends through ¹H-NMR spectroscopy. Talanta. 2017;168:121-25.
- [19] Muthukumaran C, Praniash R, Navamani P, Swathi R, Sharmila G, Kumar NM. Process optimization and kinetic modeling of biodiesel production using non-edible *Madhuca indica* oil. Fuel. 2017;195:217-25.
- [20] Hebbar HRH, Math MC, Yatish KV. Optimization and kinetic study of CaO nano-particles catalyzed biodiesel production from *Bombax ceiba* oil. Energy. 2018;143:25-34.
- [21] Feyzi M, Shahbazi Z. Preparation, kinetic and thermodynamic studies of Al-Sr nanocatalysts for biodiesel production. J Taiwan Inst Chem E. 2017;71:145-55.
- [22] Reddy C, Reddy V, Oshel R, Verkade JG. Room-temperature conversion of soybean oil and poultry fat to biodiesel catalyzed by nanocrystalline calcium oxides. Energy Fuel. 2006;20(3):1310-4.
- [23] Asikin-Mijan N, Taufiq-Yap YH, Lee HV. Synthesis of clamshell derived Ca(OH)₂ nano-particles via simple surfactant-hydration treatment. Chem Eng J. 2015;262:1043-51.
- [24] Fan MM, Huang JL, Yang J, Zhang PB. Biodiesel production by transesterification catalyzed by an efficient choline ionic liquid catalyst. Appl Energy. 2013;108:333-9.
- [25] Dai YM, Wu JS, Chen CC, Chen KT. Evaluating the optimum operating parameters on transesterification reaction for biodiesel production over a LiAlO₂ catalyst. Chem Eng J. 2015;280:370-6.
- [26] Mahesh SE, Ramanathan A, Begum KMMS, Narayanan A. Biodiesel production from waste cooking oil using KBr impregnated CaO as catalyst. Energy Convers Manage. 2015;91:442-50.
- [27] Takase M, Zhang M, Feng W, Chen Y, Zhao T, Cobbina SJ, et al. Application of zirconia modified with KOH as heterogeneous solid base catalyst to new non edible oil for biodiesel. Energy Convers Manage. 2014;80:117-25.
- [28] Keera ST, El Sabagh SM, Taman AR. Castor oil biodiesel production and optimization. Egypt J Pet. 2018;27:979-84.
- [29] Li M, Chen D, Zhu X. Preparation of solid acid catalyst from rice husk char and its catalytic performance in esterification. Chin J Catal. 2013;34:1674-82.
- [30] Reyero I, Arzamendi G, Gandía LM. Heterogenization of the biodiesel synthesis catalysis: CaO and novel calcium compounds as transesterification catalysts. Chem Eng Res Des. 2014;9(2):1519-30.
- [31] Dianursanti, Religia P, Wijanarko A. Utilization of n-hexane as co-solvent to increase biodiesel yield on direct transesterification reaction from marine microalgae. Procedia Environ Sci. 2015;23:412-20.
- [32] Akkarawatkhosith N, Kaewchada A, Jaree A. Enhancement of continuous supercritical biodiesel production: influence of co-solvent types. Energy Procedia. 2019;156:48-52.
- [33] Pan H, Li H, Zhang H, Wang A, Jin D, Yang S. Effective production of biodiesel from non-edible oil using facile synthesis of imidazolium salts-based Brønsted-Lewis solid acid and co-solvent. Energy Convers Manage. 2018;166:534-44.
- [34] Yin X, Duan X, You Q, Dai C, Tan Z, Zhu X. Biodiesel production from soybean oil deodorizer distillate using calcined duck eggshell as catalyst. Energy Convers Manage. 2016;112:199-207.
- [35] Buasri A, Chaiyut N, Loryuenyong V, Worawanitchaphong P, Trongyong S. Calcium oxide derived from waste shells of mussel, cockle, and scallop as the heterogeneous catalyst for biodiesel production. Sci World J. 2013;2013:1-7.