



Chiang Mai J. Sci. 2019; 46(5) : 987-1000

<http://epg.science.cmu.ac.th/ejournal/>

Contributed Paper

Biodiesel Production from Canola Oil and Methanol Using Ba Impregnated Calcium Oxide with Microwave Irradiation-Assistance

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Received: 17 December 2018

Revised: 4 March 2019

Accepted: 23 March 2019

ABSTRACT

In this study, powdered waste chicken (*Gallus domesticus*) eggshells, which were used as a raw calcium carbonate material, were calcined at 900 °C for 2 h in order to obtain calcium oxide (CaO). It was then impregnated by 10% by weight (wt.%) of barium (Ba) using barium chloride (BaCl₂) precursor, and subsequently calcined at 900 °C for 4 h to yield a heterogeneous Ba/CaO catalyst. The Ba/CaO catalysts were characterized by thermogravimetric analysis (TGA), X-ray diffraction (XRD), scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS), X-ray fluorescence spectrophotometer (XRF), Fourier-transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS) analyses. The prepared catalysts were applied for the transesterification of canola oil with methanol under microwave-assisted heating (300 W) to form fatty acid methyl esters (FAME). The FAME composition was analyzed using gas chromatography with flame ionization detection (GC-FID). The effects of the catalyst loading level, reaction time and methanol: canola oil molar ratio on the FAME yield were evaluated independently (univariate analysis), while the catalyst reusability was also investigated. The synthesized Ba/CaO catalyst showed a high catalytic performance with a maximum biodiesel yield of 94% when using a 3 wt.% catalyst loading, 9:1 molar ratio of methanol: canola oil for a 2 min of reaction time under 300 W microwave irradiation. Furthermore, the catalyst exhibited good reusability with a biodiesel yield of more than 90% after recycling for more than three cycles.

Keywords: biodiesel, transesterification, calcium oxide, heterogeneous catalyst, barium impregnated

1. INTRODUCTION

Due to the increased consumption rate of the limited reserves of fossil fuels and the concerns over greenhouse gas emissions from their combustion, biofuels, such as biodiesel, have become very attractive options since, for example, compared to petroleum-based diesel, biodiesel has high energy content with lower environmental emissions and produces no sulfur compounds during combustion [1-3]. Biodiesel is mainly derived from biomass resources that are renewable, biodegradable and non-toxic as well as from vegetable oils, animal fats, algae and used cooking oils as the feedstock by transesterification with an alcohol like methanol or ethanol in the presence of catalyst to yield fatty acid methyl esters (FAME) or fatty acid ethyl esters (FAEE), respectively [4-6]. In general, biodiesel can be produced using a homogeneous basic (potassium hydroxide, potassium methoxide, sodium hydroxide or sodium methoxide) or acidic (sulfuric acid) catalyst because they have a high catalytic activity even if operating under a short reaction time [7]. Nevertheless, the use of the homogeneous catalysts have many drawbacks, for example, they are difficult to separate from the reaction for reuse or regeneration, leading to the production of a large amount of contaminated cleansing water (about 10% by volume of the biodiesel) that has to be treated prior to disposal and so increases the overall cost for biodiesel production as well as causing reactor corrosion [8].

To overcome these issues, a heterogeneous catalyst is widely applied for many applications. As for biodiesel production, it can provide a high biodiesel yield [9], be easy to separate from the reaction products [10], has no toxicity or corrosion [8] as well as can be used in a continuous process and can be reused with or without regeneration [1,11]. Several materials have been tested as heterogeneous catalysts for transesterification reaction, including alkali oxides and alkali earth metal oxides supported on

silica [12], zinc oxide modified with alkali earth metals [13], basic zeolites [14,15] and biochar [16] based catalysts. Some researchers have reported that alkali earth oxide compounds have a good catalytic activity due to their high basicity, and are capable of producing a higher biodiesel conversion under mild reaction conditions with a long catalyst lifetime [2, 12, 13].

Presently, calcium oxide (CaO)-based catalysts have attracted a special interest because of the abundant availability of calcium carbonate (CaCO_3) sources (their precursor) in nature, their low corrosiveness, environmental friendliness, low cost, good catalytic performance at low temperature and pressure, easiness to handle the material and a low solubility and high basicity that can be regenerated and reused [8,11,17]. Typically, CaO-based catalysts are made by the thermal decomposition of CaCO_3 [1]. The utilization of natural calcium sources from solid waste materials, such as *Turbo jourdani* (Gastropoda: Turbinidae) [18] and eggs [5], have been used as feedstocks for CaO-based catalyst preparation.

The catalyst obtained from waste eggshells exhibited the highest catalytic performance, as well as the highest biodiesel yield [19]. The use of waste eggshells as a catalyst for biodiesel synthesis from waste cooking oil at room temperature gave a high biodiesel yield (97 wt.%), which was obtained after 11 h of regular stirring and in which the catalyst could be recycled or reused five times [20]. Likewise, the biodiesel produced from waste vegetable oil using eggshells as the solid-based heterogeneous catalyst was within the biodiesel standard specifications, where a biodiesel yield of 91% was obtained, and the catalyst showed sustained activity after being recycled and reused 10 times [21]. The basicity of CaO derived from waste *Turbonilla striatula* shells was increased by the incorporation of barium (Ba) [22] to form a solid heterogeneous Ba/CaO catalyst for the transesterification of waste cooking oil. A high catalytic activity

with a biodiesel yield of more than 98% was obtained with 1% by weight (wt.%) Ba doped CaO catalyst in a 3 h reaction time. However, the time of the process is still too long (over 3 h). Conventionally, one of the main challenges of biodiesel production is obtaining the maximum biodiesel yield under suitable conditions at the minimum production cost such as reducing the time of transesterification reaction. In the published literature, Buasri *et al.* studied the process for biodiesel synthesis from *Jatropha Curcus* oil under microwave-assisted to expedite the chemical reaction and gave a high biodiesel yields in a short time. They demonstrated that the optimum conditions, which yielded a conversion of FAME of nearly 95%, were reaction time under microwave-assisted 4 min and the catalyst was used for 3 cycles [23]. Zamberi *et al.* studied the catalytic performance of CaO derived from waste cockles on the biodiesel synthesis through microwave irradiation method. They was found that the transesterification reaction via microwave-assisted process has reduced the reaction time (4 min), which shows that it can be reduced as an energy source due to its ability in accelerating the transesterification [24]. Buasri *et al.* studies focused on using a microwave heating system to improve the FAME conversion for transesterification. The results showed that the microwave-assisted process has increased biodiesel yield, and to reduced reaction time and energy consumption. The highest biodiesel yield was obtained under the 3 min of reaction time. The FAME yield was improved due to the use of microwave heating [25]. Moreover, Jitjamnong proposed that the way to reduce the time of transesterification can be obtained by using microwave irradiation and barium loading on CaO (5–15 wt.%) [26]. However, the application of microwave irradiation for biodiesel synthesis has become more common or practical as a productive method since irradiation can increase the velocity of chemical reactions and leads to

a different selectivity, higher yield and lower energy consumption [27].

This research is mainly focused on using a microwave heating method to improve the FAME yield and reducing its synthesis time. These improvements have helped to reduce energy consumption and further contribute to lower production costs of biodiesel. In the part of increasing yield, this research examined the variables affecting the FAME yield, which consists of the ratio of methanol: canola oil, loading level of catalyst and reusability after repeated reactions. In the part of reducing synthesis time, microwave exposure time was used to shorten the oil synthesis period. Time exposure to microwave irradiation was varied (1–5 min) to find the best time that gave the highest yield of FAME. The best time was applied to the experiment of increasing FAME yield (methanol: canola oil molar ratio and catalyst loading level as well as the catalyst reusability after repeated reactions). 10 wt.% Ba/CaO was synthesized via conventional impregnation, and household microwave oven 300 W irradiation power was used. The ratio of methanol: canola oil molar (9–18:1), catalyst loading level (1–5 wt.%), and catalyst reusability (1–4 times) was varied. The physicochemical properties of the derived CaO and 10 wt.% Ba/CaO catalyst were evaluated by thermogravimetric analysis (TGA), X-ray fluorescence spectrophotometer (XRF), Fourier-transform infrared spectroscopy (FT-IR), scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS), X-ray diffractometry (XRD) and X-ray photoelectron spectroscopy (XPS).

2. MATERIALS AND METHODS

2.1 Materials

Commercial canola oil was obtained from Lam Soon Public Company Limited, Thailand, and used as the feedstock for FAME production with methanol (analytical reagent grade). Waste chicken eggshells were collected from the

domestic waste in Songkhla, Thailand and used to prepare CaO. Barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$; 99%) was purchased from Ajax Finechem Pty. Ltd. was used as the Ba doping precursor.

2.2 Catalyst Preparation

For the synthesis of CaO, the waste eggshells were cleaned with distilled water to remove the adsorbed organic materials and other impurities, followed by drying in an oven at 120 °C overnight. Subsequently, the dried waste eggshells were pulverized and calcined in a furnace at 900 °C under the atmosphere at a heating rate of 10 °C/min for 2 h to obtain the white-colored CaO powder. The Ba/CaO catalyst was prepared by incipient wetness impregnation using BaCl_2 precursor for 24 h at a Ba loading level of 10 wt.%. Afterward, the impregnated catalyst was dried in an oven overnight to remove the adsorbed water, and subsequently calcined at 900 °C at a heating rate at 10 °C/min for 4 h. The Ba/CaO catalyst was preserved in a desiccator to avoid subsequent interaction with moisture and carbon dioxide (CO_2) in the ambient air.

2.3 Catalyst Characterization

The thermal decomposition of the CaO obtained from waste eggshells and derived Ba/CaO catalyst was determined by TGA using a Perkin-Elmer TGA7 thermal gravimetric analyzer. The sample was placed in an aluminum pan, and the heating was conducted under a nitrogen atmosphere from room temperature to 1000 °C at a rate of 20 °C/min.

The surface morphology of all catalysts, after gold coating by sputtering, was investigated using SEM-EDS analysis (Oxford Aztec model) at 500× magnification with an accelerating voltage of 2.0 kV.

The actual element composition of the catalyst (Ca, O, C, Ba, and Mg) was evaluated by XRF analysis using a Philips, power 2400 model. The chemical functional group of the

neat CaO was observed by FT-IR analysis using a Thermo Nicolet Nexus 670 FTIR spectrometer. The solid sample and potassium bromide (KBr) powder were placed on the monolithic diamond crystal plate. The spectrum was collected on a Perkin-Elmer spectrometer. The IR spectrum was operated at 4 cm^{-1} resolution in absorbance mode for 32 scans over a spectral frequency range of 4000–650 cm^{-1} .

The composition of the crystalline phases of the CaO support and Ba/CaO catalyst was investigated using XRD analysis. The patterns of the samples were identified on Rigaku X-ray diffractometer using $\text{CuK}\alpha$ radiation electrons of wavelength $\lambda = 1.5405 \text{ \AA}$ and operated at 40 kV and 30 mA. Samples were run in a continuous scan mode at a 2θ range of 10° to 90° with the scanning speed of 5° per second.

The phase composition at the surface of the CaO and Ba/CaO catalysts was evaluated by XPS analysis (Kratos Axis Ultra DLD). The incident radiation was operated by a monochromatic Al $\text{K}\alpha$ (1486.6 eV) source at 15 kV with the residual pressure lower than 5×10^{-7} torr in the analyzer chamber. The standard practice in XPS spectra was calibrated using hydrocarbon C1s line with binding energy (BE) of 284.6 eV.

2.4 Transesterification of Canola Oil

Canola oil (100 g) was added in a 500-mL glass reactor and placed on a hot plate at 60 °C. The desired amount of catalyst (1–5 wt.% compared to the starting vegetable oil) and methanol (9–18:1 molar ratio of methanol: canola oil) were then added into the reactor with stirring at 300 rpm. After 10 min of transesterification, the stirrer was removed and the mixed solution was transferred into a household microwave oven and irradiated at 300W for 1–5 min. The catalyst was then filtered from the mixture solution, whereas the products were poured into a separatory funnel and left overnight for phase separation.

The upper biodiesel phase was washed with deionized water at 60 °C until the pH of the washed water was neutral (pH=7). The obtained FAME was kept in a glass bottle containing anhydrous sodium sulfate to remove the humidity and then its composition was identified by gas chromatography (GC; Hewlett Packard gas chromatograph 5890 Series II) equipped with a flame ionization detector (FID) and using helium (99.99%) as the carrier gas at a flow rate of 70 mL/min. The injector and detector temperature were set at 200 °C with a split ratio of 75:1 and 230 °C, respectively. A 0.2 μ L sample of the biodiesel was injected at an oven temperature of 130 °C. After an isothermal period of 2 min, the GC oven was increased to 220 °C with a heating rate of 2 °C/min and held for 15 min. The cycle analysis time lasted for 62 min. Meanwhile, the used catalyst was washed with hexane to remove the glycerol, triglyceride, and biodiesel, dried overnight in an oven and then reused in the next reaction to evaluate the catalyst reusability.

3. RESULTS AND DISCUSSION

3.1 Catalyst Characterization

In order to evaluate the thermal stability of the calcined waste eggshells, TGA was performed over a heating range of 27–1000 °C at a heating rate of 20 °C/min (Figure 1). Two mass losses of a total weight loss of about 9.98% were observed. The first weight loss step at 50–450 °C was about 8.80% and was attributed to the evaporation of free moisture and the decomposition of calcium hydroxide ($\text{Ca}(\text{OH})_2$) to be CaO and H_2O . The second weight loss stage of 1.18% around 490–750 °C, corresponding to the removal of CO_2 from CaCO_3 as it transformed into CaO. The TGA profile of the catalyst did not change at the temperature over 800 °C, indicating that the transformation of CaCO_3 to CaO was complete. Thus, a calcination temperature 900 °C for 2 h was sufficient to convert the CaCO_3 from waste eggshells to CaO.

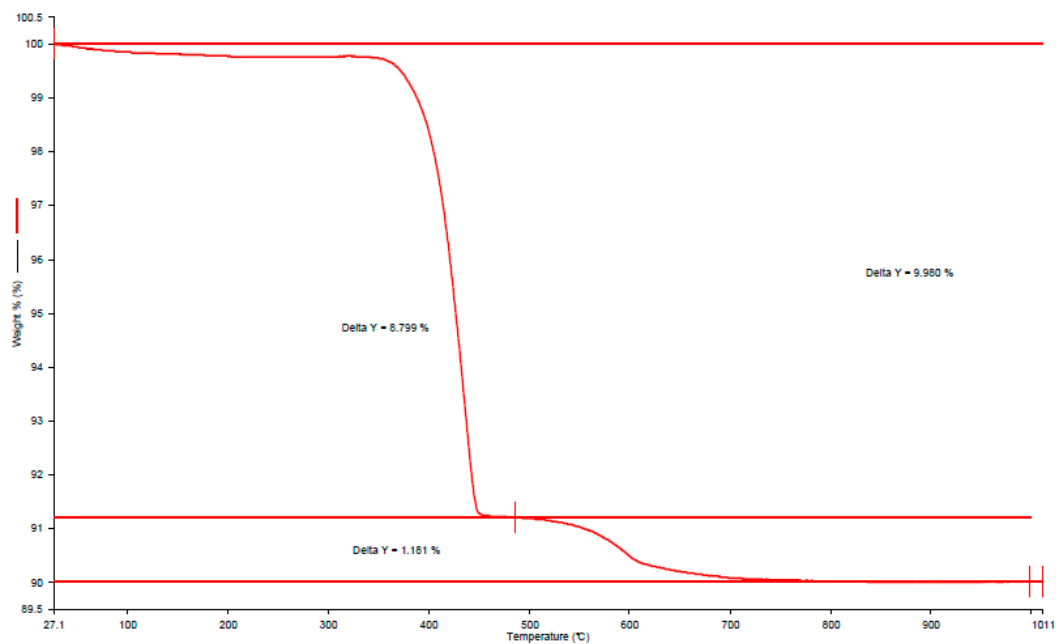


Figure 1. Representative TGA profile of the CaO derived from waste chicken eggshells.

The surface morphology of the CaO support and Ba/CaO catalyst was analyzed by SEM-EDS (Figure 2). The CaO showed clustered and spherical shapes, where the surface was rough and agglomerated with variable morphologies. This might be caused by the breakdown of the organic matter in the waste eggshells during the calcination at 900 °C for 2 h, which changed the crystallinity of CaCO₃ into the high porosity of CaO [18]. Figure 2B displays the spherical shapes of the Ba/CaO catalyst, where the particle formation was changed from large agglomerate shapes in CaO to the well-dispersed particles in the Ba/CaO, which might be the Ba supported on CaO calcined at 900 °C for 4 h. It was clearly

observed that the Ba was deposited on the CaO support, indicating a strong basic active site for the transesterification reaction.

The qualitative element of Ca, O, C, Ba, and Mg in the CaO support and Ba/CaO catalyst were evaluated by SEM-EDS (Figure 3), whereas the quantitative results are summarized in Table 1. For CaO support, it was noteworthy that the major components were Ca (54.2%) and O (40.7%), whilst a minor content was C (4.7%), supporting the decomposition of CaCO₃ into CaO. For Ba/CaO catalyst, it was shown that the elements were Ca (54.6%), O (42.5%), and Ba (2.9%), respectively. This result was strongly consistent with the XRF analysis (Table 1).

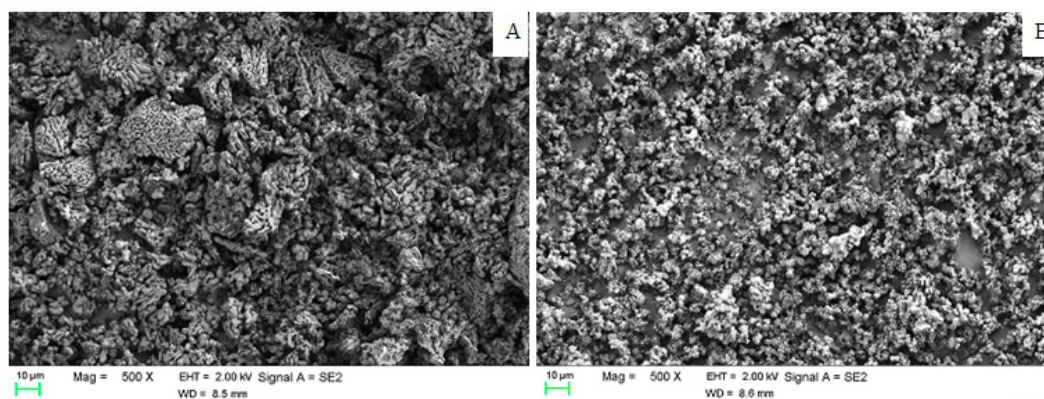


Figure 2. Representative SEM images of the (A) CaO derived from waste chicken eggshells and (B) Ba/CaO catalysts.

Table 1. Elemental composition of the synthesized CaO catalysts.

Element	Concentration (%) ^a	Concentration (%) ^b
Ca	54.2	63.10
O	40.8	30.11
C	4.6	2.78
N	- ^c	2.86
Mg	0.4	0.57

^a Determined by ^aSEM-EDS or ^b XRF and analyses

^c Below the limit of detection

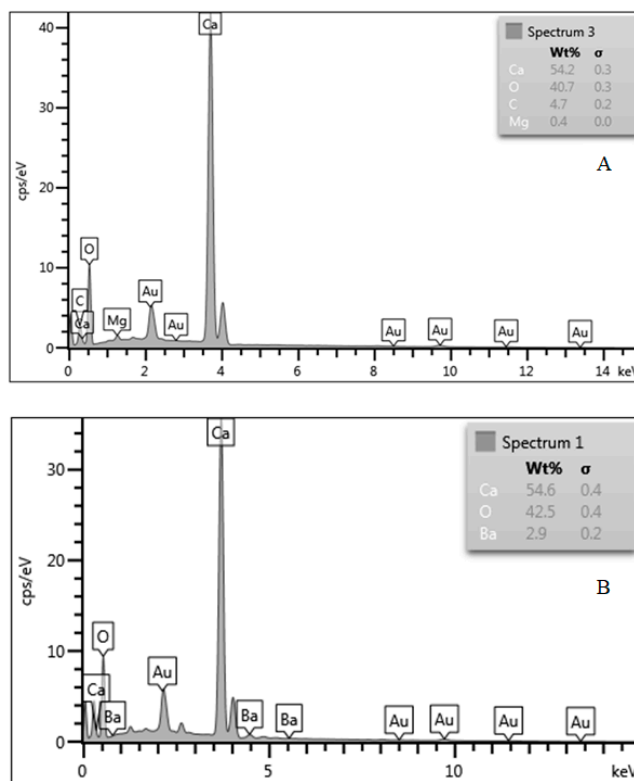


Figure 3. Representative SEM-EDS photographs of the (A) CaO and (B) Ba/CaO catalysts.

The FT-IR pattern of the waste eggshell derived CaO support and the 10 wt.% Ba/CaO catalyst over the range of 650–4000 cm^{-1} is shown in Figure 4. The spectrum peak at 871 cm^{-1} in the CaO support was assigned to the out of plane vibration modes of the carbonate (CO_3^{2-}) group, while the C-O stretching vibration appeared as a strong at 1054 cm^{-1} and a weak peak at 1093 cm^{-1} . The asymmetric stretching of the C=O group in CO_3^{2-} ions was clearly exhibited near 1444 cm^{-1} . The strong peak at 3641 cm^{-1} corresponded to the hydroxyl group stretching peak of hydroxide species, which was attributed to the absorption of water on the synthesized catalyst surface [28]. Moreover, the characteristic O-H stretching vibration was shown at 3720 cm^{-1} .

In the case of the Ba/CaO catalyst, the broad absorption peak at 871 cm^{-1} disappeared

due to the calcination stage causing the catalyst to lose CO_3^{2-} ions, which also supported the complete decomposition of CaCO_3 to CaO. After 10 wt.% Ba was loaded on the CaO, the broad peak at 1444 cm^{-1} became narrower and shifted at 1417 cm^{-1} , which showed the presence of the asymmetric stretching vibration of BaO. The appearance of an absorption band at 1613 cm^{-1} and a broader band at around 3423 cm^{-1} were attributed to the bending mode of the OH group of physically adsorbed moisture on the surface, and the vibration of the O-H group became broader with the progressive replacement of Ba on the surface [10].

Powder XRD patterns of the CaO support and the 10 wt.% Ba/CaO catalyst are illustrated in Figure 5. The catalysts exhibited sharp peaks, which showed a high degree of crystallinity. The CaO support showed prominent spectra

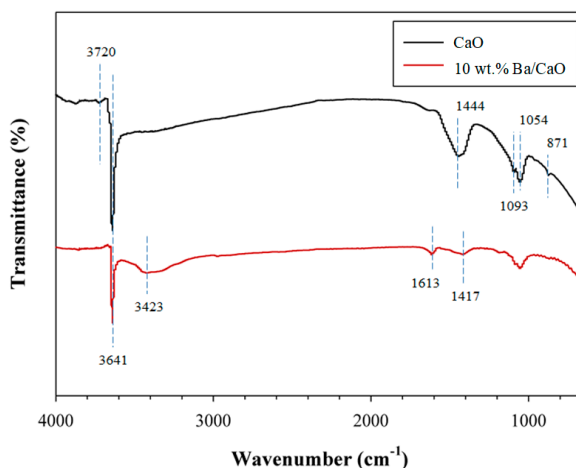


Figure 4. Representative FTIR spectrum of the CaO and Ba/CaO catalysts.

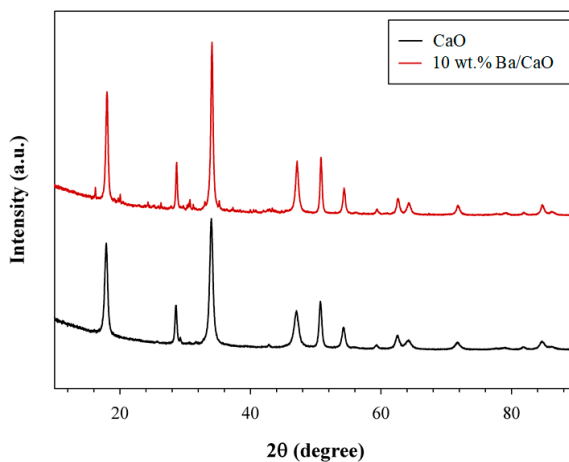


Figure 5. Representative XRD patterns of the CaO and Ba/CaO catalysts.

peaks at a 2θ of 33.98° , 46.98° , 54.25° and 62.45° that corresponded to the (111), (200), (220) and (311) planes of CaO, respectively, supporting that the calcination at 900°C for 2 h caused the complete transformation of CaCO_3 to CaO, consistent with the TGA results. The 10 wt.%Ba/CaO catalyst showed no significant shifts in the baseline peaks compared with those of CaO support. The main reflection pattern depicted intensified peaks that were observed at a 2θ at 34.08° , 47.02° , 54.37° , and 62.49° , which corresponded to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) crystallographic planes of CaO,

respectively. The peak of barium oxide (BaO) was not observed in the diffraction pattern due to the d value for the diffraction peak of the BaO tetragonal crystal structures being very close to the cubic CaO phase [10].

The surface species of the CaO support and Ba/CaO catalyst were determined by wide and narrow scan XPS analysis, as shown in Figure 6. For the CaO support, the 2p XPS spectra of Ca elements exhibited one strong peak at a BE of 350 eV. One peak at O 1s signal centered at 531 eV, which was assigned to the presence of oxygen elements in the Ba/

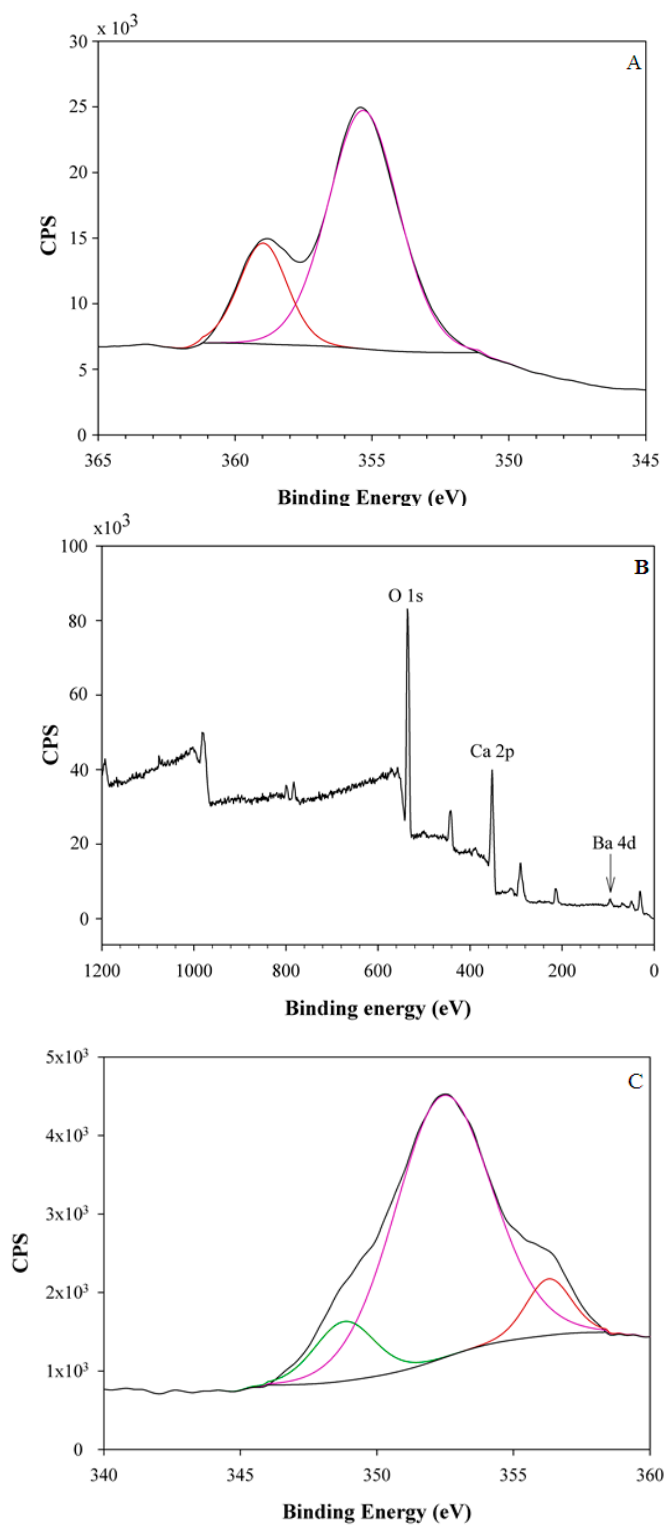


Figure 6. Representative XPS spectra of the (A) CaO, (B) Ba/CaO (narrow scan mode) and (C) Ba/CaO for Ca 2p species.

CaO particles during calcination at 900 °C (Fig. 6B). Considering the Ba/CaO catalyst with a narrow scan mode (Figure 6B), although the BE of the Ba 4d peak was detected at 88 eV it was only a small peak and so it was concluded that BaCl₂·2H₂O was the predominant species on the surface of the Ba/CaO catalyst after calcination. The result was concordant with the results reported by Karshoğlu et al. [29]. The BE of Ba/CaO for the Ca 2p species was in the range of 352 eV (Figure 6C). The result was confirmed by SEM-EDS, XRF and XRD analyses.

3.2 Catalytic Efficiency of the 10 wt.% Ba/CaO Catalyst in The Transesterification of Canola Oil with Methanol

The composition of the FAME obtained from canola oil reacted with methanol using a 3 wt.% catalyst loading, 9:1 methanol:

canola oil molar ratio and 2 min microwave reaction time were determined by GC-FID analysis (Table 2). The biodiesel composition was categorized as saturated, mono-, di- and tri-unsaturated FAMES. When using the pure CaO support, the monounsaturated FAME was the main composition around 61.6%, whereas the total FAME composition was about 89.5%. Interestingly, the total FAME yield using the Ba/CaO catalyst significantly increased to 94.33%, with a different composition, especially with the two-fold higher level of tri-unsaturated FAMES, due to the Ba ions being more active in the transesterification reaction due to their stronger basic strength [10]. The result showed that the using of Ba/CaO from waste eggshells can improve yield to achieve over than 94% yield, while a household microwave oven was used at 300 W irradiation power to give a high biodiesel yield in short reaction time.

Table 2. FAME composition of the canola oil biodiesel, as determined by GC-FID analysis.

FAME composition (%) ^a	CaO	10 wt.% Ba/CaO
Saturated FAME	2.75	4.35
Monounsaturated FAME	61.62	59.82
Diunsaturated FAME	19.16	18.84
Triunsaturated FAME	5.98	11.32

^a Conditions: catalyst loading 3 wt.%, 65 °C, methanol: oil molar ratio of 9:1 and 2 min microwave irradiation (reaction) time.

3.3 Effect of The Operating Parameters on The FAME Yield: Univariate Optimization

3.3.1. Effect of the catalyst loading level

The effect of different Ba/CaO catalyst loading levels (1–5 wt.%) on the transesterification of canola oil with methanol was evaluated at a constant 9:1 molar ratio of methanol: oil at 65 °C, for 2 min microwave-assisted transesterification (Figure 7). Increasing the catalyst dosage from 1 to 2 wt.% decreased the obtained biodiesel yield from 93.56% to 92.64%, which might be

due to the poor mixing of the heterogeneous catalyst and reactants [2]. However, the FAME yield increased at higher catalyst loading levels, with a maximum conversion level of 94.33% being obtained at a catalyst dosage of 3 wt.%. The increased FAME yield from 2 to 3 wt.% catalyst loading reflects the increased number of available basic sites from the catalyst to interact with the reactants. However, the FAME yield slightly dropped when catalyst levels were above 3 wt.%, which was caused by the catalyst

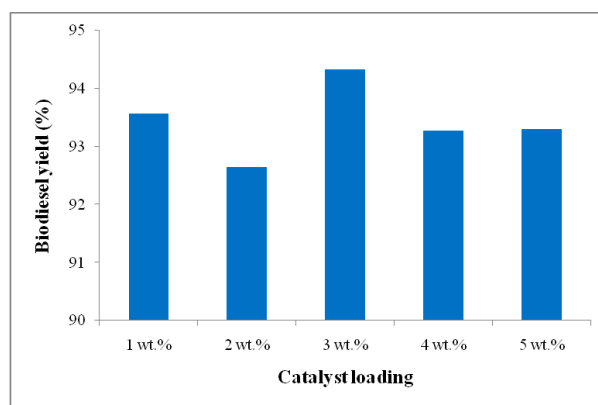


Figure 7. Influence of different Ba/CaO catalyst loading levels (wt.%) on the obtained FAME yield (conditions: methanol: oil molar ratio 9:1, 65 °C and 2 min microwave irradiation (reaction) time).

concentrations resisting efficient mass transfer between the reactants and catalyst phase [7], and also the solution became too viscous for adequate mixing [17]. Accordingly, the optimal catalyst loading level was 3 wt.%.

3.3.2. Effect of the methanol: canola oil molar ratio

The effect of the methanol: canola oil molar ratio was investigated using 3 wt.% catalyst loading level and operated at 65 °C for 2 min in the microwave (Figure 8). A methanol: oil molar ratio of 9:1 gave a maximum FAME yield of 94.33%, since sufficient excess methanol was present to shift the equilibrium to the forward transesterification reaction [30]. However, the biodiesel yield was 92.54%, 92.61%, and 92.45% when the methanol: oil molar ratio was increased to 12:1, 15:1 and 18:1, respectively. This was due to the excess methanol diluting the reaction mixture, leading to a lower contact between the catalyst surface and triglycerides [2]. Therefore, methanol: oil molar ratio of 9:1 was considered for further study.

3.3.3. Effect of the reaction time

The effect of the microwave irradiation (reaction) time (1, 2, 3, 4 and 5 min) on the

FAME yield was evaluated using 3 wt.% catalyst loading level at 65 °C and 9:1 molar ratio of methanol: canola oil (Figure 9). The FAME yield was over 93% within 1 min, where a maximum FAME yield around 94% was obtained at longer reaction time. Thus, the 2-min reaction time under microwave radiation was adequate for the transesterification reaction in this study [31].

3.4 Effect of Catalyst Reusability

The major advantage of heterogeneous catalyst over the homogeneous catalyst is its reusability for multiple reaction cycles. Thus, the synthesized Ba/CaO heterogeneous catalyst was examined for their performance on the transesterification of canola oil with methanol in terms of the FAME yield. The reactions were performed under the same conditions which were 3 wt.% catalyst loading level, 9:1 molar ratio of methanol: canola oil, reaction temperature at 65 °C, agitation speed at 300 rpm and 2 min of 300 W microwave power. After the transesterification, the solid Ba/CaO catalyst was separated from the reaction mixture, washed, dried and reused in the next reaction. At the 1st reaction cycle, the FAME yield was around 94% and then gradually decreased to 90% after the 3rd reaction cycle (Figure 10). At the

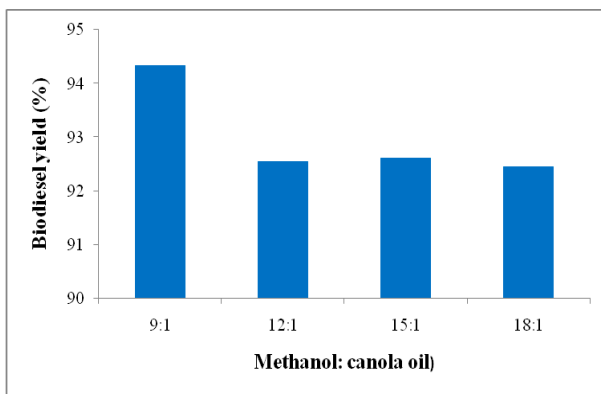


Figure 8. Effect of the methanol: canola oil molar ratio on the obtained FAME yield (conditions: catalyst loading 3 wt.%, 65 °C and 2 min microwave irradiation (reaction) time).

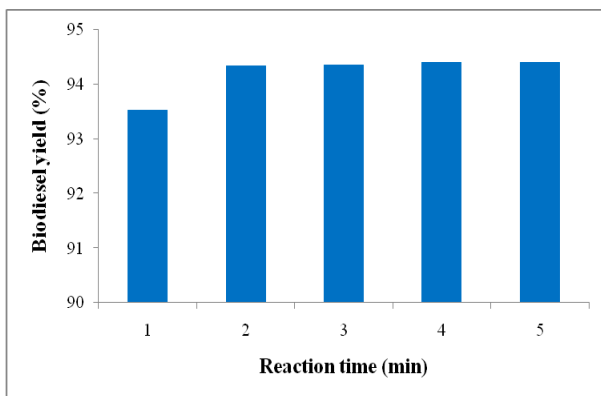


Figure 9. Effect of the microwave irradiation (reaction) time on the obtained FAME yield (conditions: catalyst loading 3 wt.%, 65 °C and methanol: oil molar ratio of 9:1).

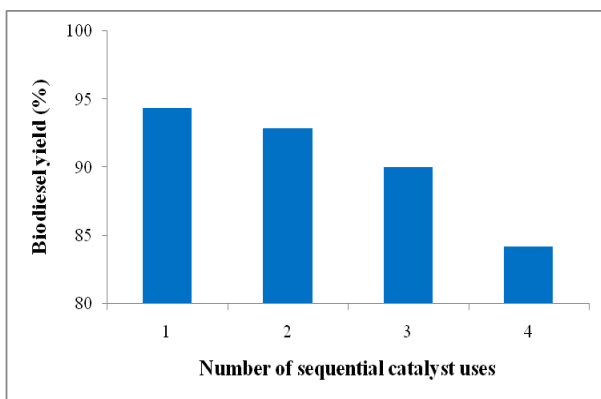


Figure 10. Reusability of the Ba/CaO catalyst in terms of the obtained FAME yield (conditions: catalyst loading 3 wt.%, 65 °C, methanol: oil molar ratio of 9:1 and 2 min microwave irradiation (reaction) time).

4th reaction cycle, nevertheless, the FAME yield was merely 84%. This decrease likely reflects that during the recovery process moisture and CO₂ in the air transform the CaO species to Ca(OH)₂ and CaCO₃, which have a lower basicity [28].

4. CONCLUSIONS

Powdered waste chicken eggshells were successfully used as the source of CaO catalyst for biodiesel production by calcination at 900 °C for 2 h, resulting to the complete converting of CaCO₃ to CaO. After 10 wt.% Ba was loaded on the CaO by incipient wetness impregnation, the optimal reaction conditions at 65 °C for the transesterification of canola oil with methanol to FAME was found (by univariate analysis) to be a 3 wt.% catalyst loading, 9:1 molar ratio of methanol to canola oil and 2 min reaction time under 300 W microwave irradiation. The microwave irradiation has helped to reduce the synthesis time in transesterification. The advantage of this method has many advantages in biodiesel synthesis. It is cost effective and it can be employed as an energy source. In addition the transesterification via microwave-assisted chemical reactions was better than those obtained using other synthetic techniques due to it can increase the reaction rate. Moreover, the Ba/CaO catalyst showed a high catalytic performance giving a maximum FAME yield of 94% and could be reused for three cycles, maintaining the FAME yield of more than 90%.

ACKNOWLEDGMENTS

The author gratefully acknowledges the financial support given to him by Rajamangala University of Technology Srivijaya, Songkhla, Thailand. Likewise, he is deeply thankful to Ms. Chachchaya Thunyaratchatanon and Ms. Chatrawee Direksilp, Ph.D. students at The Petroleum and Petrochemical College, Chulalongkorn University, Thailand for assisting him with instrumental analysis.

RESEARCH HIGHLIGHTS

- Calcium oxide as a heterogeneous catalyst was derived from waste chicken eggshells.
- 10 wt.% of Ba was loaded on the calcined CaO catalyst.
- Household microwave oven (300 W) assisted production of biodiesel was performed.
- Influence of reaction time, methanol: canola oil molar ratio, catalyst loading level, and catalyst reusability were studied.

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