



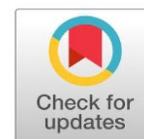
Original Research Article

Transesterification of rendered chicken fats catalyzed by waste chicken eggshells for biodiesel production

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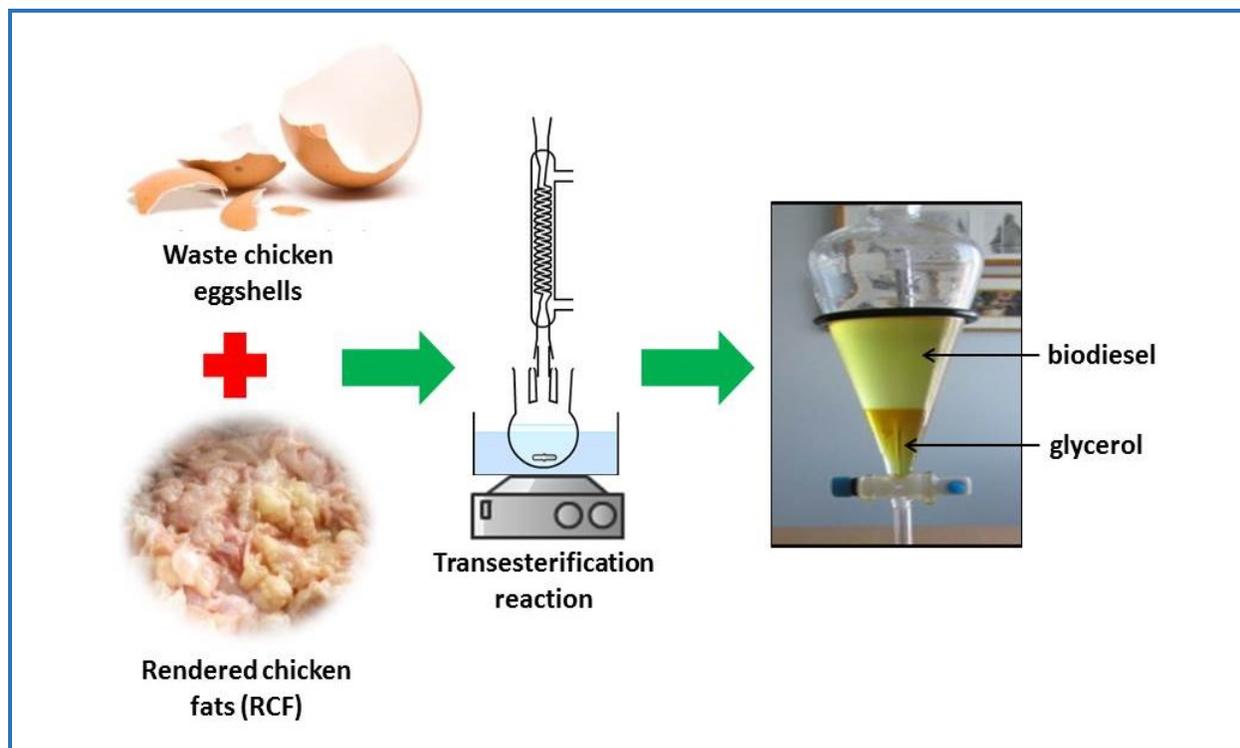
Rendered chicken fats
Waste chicken eggshells
Transesterification

ABSTRACT

To make the biodiesel competitive with petroleum diesel, cheap and abundant materials can be utilized as a catalyst and waste oils can be used as resources. In this research study, the potential of waste chicken eggshells was used as a catalyst to produce biodiesel from the rendered chicken fats (RCF). The calcium methoxide catalyst was prepared by calcining the waste eggshells at 900 °C in air for 4 h followed by treatment with methanol under reflux condition. The physico-chemical properties of the prepared catalyst were characterized using the X-ray diffraction (XRD) analysis, Brunner-Emmet-Teller (BET), field emission scanning electron microscopy (FE-SEM), and temperature programmed desorption of carbon dioxide (CO₂-TPD). Two-step process including, esterification and transesterification were employed to convert the RCF to fatty acid methyl ester (FAME). Esterification pretreatment with ferric sulfate successfully reduced 75.1% of the FFA content in RCF which enables high biodiesel production. Under the optimal reaction condition, the highest conversion of biodiesel was found to be 90.04% at 1:15 oil to methanol molar ratio, 3 wt% catalyst loading, and 2 h reaction time at 65 °C. The catalyst was successfully used for 4 consecutive cycles with less than 2 mg/kg of Ca was detected in the product.

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Graphical Abstract



Introduction

Nowadays, biodiesel is considered the most widely used renewable fuel for motor vehicles all over the world. The global market survey has shown a skyrocketing demand for biodiesel due to its non-toxic and environmentally benign compared to that of the fossil fuel. Biodiesel which has physical and chemical characteristics similar to the diesel fuel has high flash point, high cetane number, and better lubrication. Since most of the commercial biodiesel nowadays is produced from plant oils, it does not contain sulfur, particulate matter of unburnt hydrocarbons, and other greenhouse gases (GHG) that is normally produced when dealing with a conventional engine that runs on diesel fuel.

Majority of commercial biodiesel or fatty acid methyl ester (FAME) is produced from edible oils such as soybean, palm, rapeseed, and sunflower oil through transesterification reaction in alcohol (mainly methanol) at the presence of homogeneous or heterogeneous catalysts [1]. Studies have shown that the use of base catalysts including, sodium methoxide, potassium hydroxide, sodium hydroxide, and calcium-based catalysts were extensively reported as a most efficient catalyst in the transesterification reaction for the production of biodiesel. Calcium methoxide for instance, has been reported to yield almost 98% biodiesel within 2 h reaction of soybean oil with methanol [2]. However, an issue has been raised in terms of the use of edible oils as the source of biodiesel. The use of edible

oil has raised the food price, causing a shortage in food supply. This issue has driven researchers to find other alternatives sources of biodiesel from non-edible and used oils. The *Jatropha curcas* (*Jatropha* oil), *pongamia pinnata* (Karanja oil), *Azadirachta indica* (neem seed oil), *Hevea brasiliensis* (rubber seed tree oil), microalgae oil, are the non-edible oil resources that have been extensively studied. In addition, low cost feedstock such as waste cooking oil (WCO) and waste animal fats (WAF) have received considerable attention as biodiesel sources.

Animal fats are waste materials that are substantially cheaper than vegetable oil and it is not edible for human. It is normally used as animal feed or utilized in producing soap and wax [3]. Using animal fats such as pork lard, beef tallow, and chicken fat for biodiesel is a good alternative for recycling these wastes. However, the production of biodiesel from animal wastes is not as simple as vegetable oils. This is due to the fact that animal wastes contains high free fatty acid (FFA) that will cause soap formation and separation problem when catalyzed by the base catalysts [4]. Studies have shown that the amount of FFA contains oil should not exceed 1% for alkaline-catalyzed transesterification which corresponds to an acid value of 2 mg KOH/g [3]. For oils that contain high FFA, acid-catalyzed pre-treatment is necessary to reduce the FFA content to less than 1%, followed by transesterification with alkaline catalyst to complete the reaction.

In this study, rendered chicken fats (RCF) were esterified with acid catalyst to reduce the FFA content before undergone transesterification with solid based catalyst that was produced from waste chicken eggshells. The effect of catalyst loading, methanol to oil molar ratio and reaction time were also investigated.

Experimental

Catalyst preparation

Waste chicken eggshells were collected from the local market at Serdang, Selangor Malaysia. The outer and inner layer of the waste eggshells was washed and rinsed several times with water to remove all the impurities. Then, it was dried under sunlight, ground and sieved (250 μm) and dried at 120 °C for 12 h. The fine powder was calcined at 900 °C in air for 4 h to transform it to the oxide form. The calcium oxide was later mixed with methanol in reflux condition at 65 °C and stirred for 2 h. Finally, the modified catalyst was separated by filtration, dried at 120 °C for 2 h and kept in a desiccator.

Catalyst characterization

Thermogravimetric analysis (TGA) was used to determine phase transition and decomposition temperature of waste chicken eggshells. TGA was conducted using mettler thermogravimetry

analyzer in N₂ atmosphere from 50 °C to 900 °C (heating rate: 10 °C/min). X-ray diffraction (XRD) was used to identify the crystalline phase of the prepared catalysts was recorded on Shimadzu XRD-6000 diffractometer (Cu-K α radiation) at 30 kV. The XRD patterns were analyzed using the Joint committee on powder diffraction standards (JCPDS) file to identify the phases present in the samples. The morphology of the all catalysts before and after modification was observed using a field emission scanning electron microscope (FESEM, model LEO 1455 VP) operated at 30 kV. Prior to analysis, the samples were coated with a thin layer of aurum using BIO-RAS sputter coater. The surface area of the catalysts was determined by Brunauer-Emmer-Teller (BET) method based on the adsorption-desorption of N₂ gas at -196 °C using quantachrome ASI win automated gas sorption instrument. The basicity of the catalyst was estimated using temperature-programmed desorption of CO₂ (TPD-CO₂) conducted on thermo finnigan TPDRO 110 instrument.

Esterification reaction

The esterification reaction was conducted on double neck round bottom flask equipped with a thermometer and reflux condenser in which solid ferric sulfate, Fe₂(SO₄)₃ was used as acid catalyst. The methanol and rendered chicken fats oils with a ratio of 20:1 was mixed at 65 °C and stirred for 60 min. After the reaction was done, the catalyst was separated and the liquid mixture was left overnight to form two separate layers. The bottom layer consisting of chicken fats and esterified FFA was collected while the upper layer which consists of mixture of methanol and water was discarded. The acid value of the esterified chicken fats was recorded.

Transesterification reaction

A typical transesterification reaction was carried out in the oil bath by mixing the esterified RCF, catalyst, and ethanol in a round bottom flask. The reactor was equipped with a thermometer, mechanical stirrer, and a condenser. The molar ratio of methanol to oil was studied from 5 to 20, while the amount of the catalyst was varied from 1 to 4 wt%. The reaction mixture was stirred and heated at 65 °C for 0.5, 1, 2, and 3 h. After the reaction proceeded for the set period of time, the catalyst was separated from the mixture by centrifugation and the methanol was removed by evaporation. The biodiesel and glycerol were separated and the biodiesel conversion was calculated based on the amount of glycerol produced [5, 6]. The leaching of calcium catalyst was determined using the atomic absorption spectroscopy (AAS).

Results and Discussion

Catalyst characterizations

Thermal analysis was conducted to find the calcination temperature to transform the raw waste eggshells that mainly consists of calcium carbonate to calcium oxide. As seen in Figure 1, the decomposition of the waste chicken eggshells started at above 200 °C which attributed to loss of organic matter and chemisorbed water [7]. More significant weight loss was observed at above 600 °C which associated to the main decomposition of CaCO_3 to CaO followed by evolution of CO_2 [8]. Complete transformation of calcium carbonate was obtained at above 800 °C with a total loss of 46.50 wt% from its initial weight.

The phase transformation was further confirmed by XRD analysis. Figure 2 depicts the calcined waste chicken eggshells (calcium oxide) and the modified catalyst (calcium methoxide) after undergone modification in methanol. The XRD pattern of the CaO showed clear and sharp peak at $2\theta = 32.4^\circ, 37.6^\circ, 54.2^\circ, 64.2^\circ, 67.8^\circ$ and 79.8° (JCPDS no: 00-001-1160), indicating that calcination at 900 °C has successfully transformed the calcium carbonate to oxide form [8].

Figure 1. TGA results of the raw waste chicken eggshells

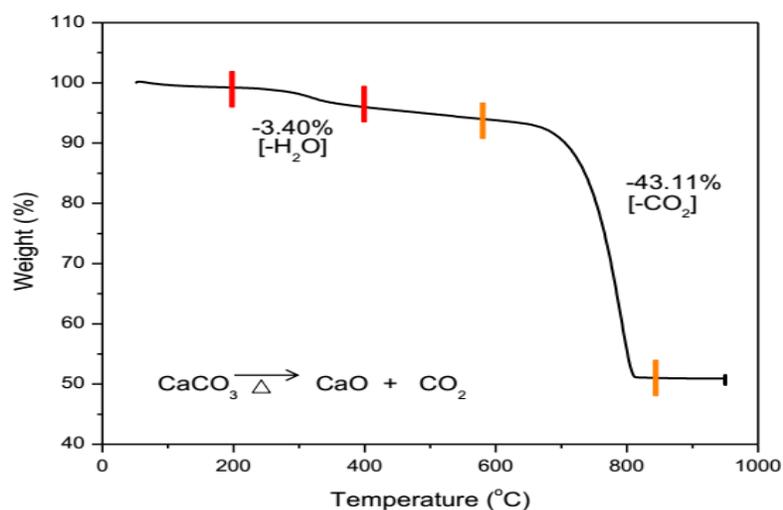
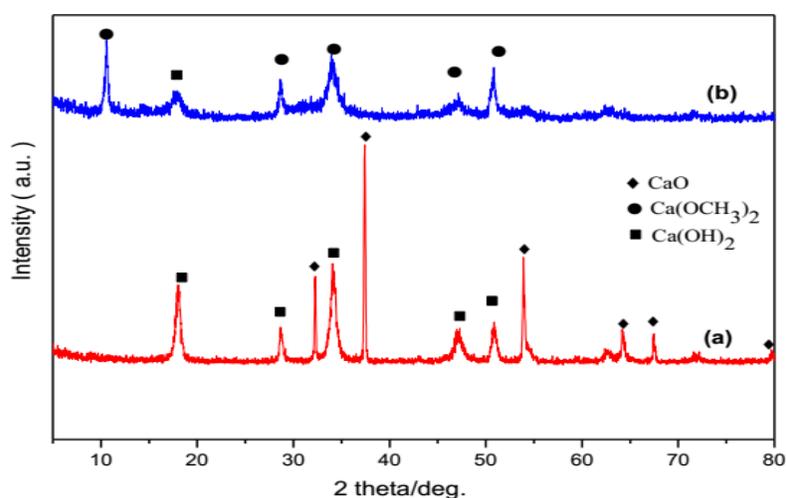


Figure 2. XRD pattern of a) calcined and b) modified catalyst



Upon modification with methanol, peaks were observed at 10.6°, 28.7°, 34.0°, and 50.9°. The peaks were identified as Ca(OCH₃)₂ phase (JCPDS no:00-020-1565) has been reported previously by Kouzu et al. [9]. Other peaks at 17.9° and 47.0° were assigned at the presence of Ca(OH)₂ phase (JCPDS no: 00-001-1079).

Table 1 summarizes the surface area, crystallite size, and the amount of the CO₂ desorbed from both calcined and modified catalysts. The calcination of fresh chicken eggshells led to small surface area and bigger crystallite size of CaO compared to Ca(OCH₃)₂. The calcined eggshell has small surface area as it has dense and pack morphology with low porosity and low pore volume (Figure 3) as previously reported by Wei et al. [8] and Khemtong et al. [9]. Obviously, the morphology of the catalysts viewed by FESEM revealed that the bulk agglomerate of dense structure (Figure 3a and b) was transformed to flakes resembling flower-like cluster structure (Figure 3c and d) when CaO was modified in methanol (Ca(OCH₃)₂). Similar image was also reported elsewhere when calcium oxide was treated with methanol [10].

Meanwhile, TPD-CO₂ analysis was used to measure the basic sites and strength of the catalyst. The higher the value of the CO₂ desorbed at high temperature, suggesting the better strength of the basic sites of the catalyst. Several studies have reported that basicity of the catalyst is one of major factor that improve the transesterification reaction [11]. The CO₂ desorption band at around 100 to 500 °C area assigned as interaction of CO₂ with sites of weak and medium basic strength. Whereas, the CO₂ desorbed at higher temperature ~600 °C can be attributed to the stronger basic sites [11, 12]. Based on Table 1, the calcined catalyst recorded inferior which was only 2.0 μmol/g. While, the total amount of CO₂ being desorbed from the modified Ca(OCH₃)₂ catalyst was 10401.2 μmol/g suggesting that modification of CaO with methanol has increased the basic strength of the catalyst with two types of basic sites (Figure 4).

Table 1. Surface area, crystallite size, and amount of CO₂ desorbed on the fresh and modified catalyst

Catalyst	Surface area (m ² /g)	Crystallite size (nm)	Amount of CO ₂ desorbed (μmol/g)	Temperature of CO ₂ desorbed, T _{max} (°C)
Calcined catalyst, CaO	5.5	41.9	2.0	573
Modified catalyst, Ca(OCH ₃) ₂	21.5	14.4	6718.8	T _{max} ¹ 503
			3682.4	T _{max} ² 703

^a Calculated from Scherrer's equation form XRD analysis

^b BET surface area

^c Calculated from TPD-CO₂ analysis

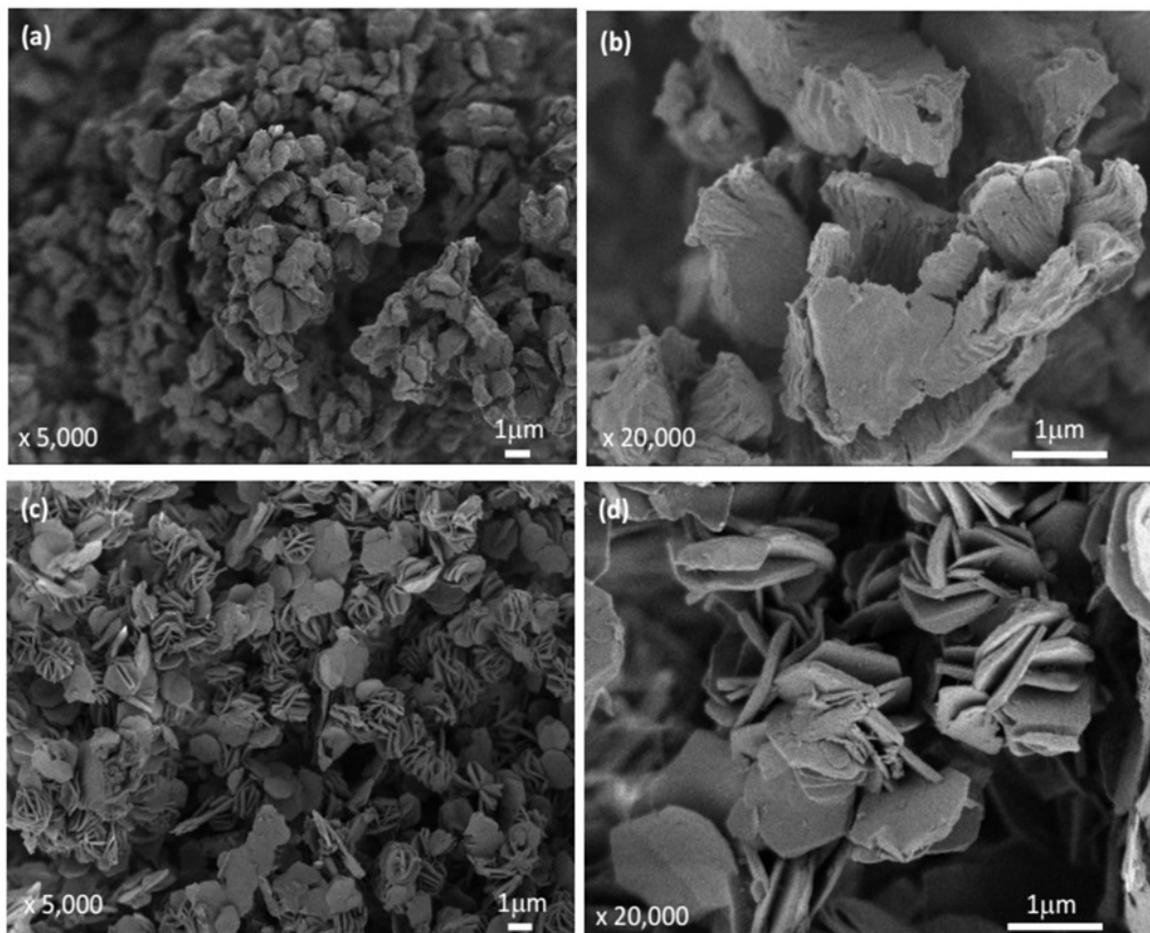


Figure 3. FESEM micrograph of calcined CaO (a and b) and modified $\text{Ca}(\text{OCH}_3)_2$ (c and d) at different magnifications

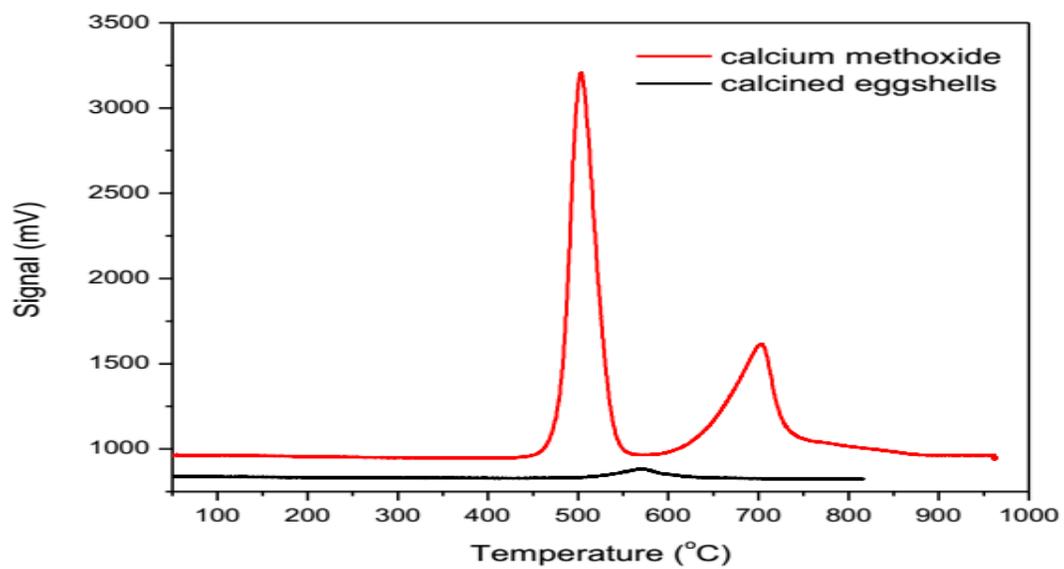


Figure 4. The TPD- CO_2 profiles for calcined eggshells (CaO) and calcium methoxide ($\text{Ca}(\text{OCH}_3)_2$)

Catalytic activity

Many studies reported that the basic catalyst could not work well in the feedstock, containing high FFA than 1.0% [13]. Thus, the rendered chicken fats were treated with ferric sulfate in esterification reaction to lower down the FFA value. After the treatment, the FFA value of the RCF was decreased from 2.53% to 0.69% which is sufficient for transesterification reaction. The oxide and modified catalyst were subsequently tested for their catalytic activity in the transesterification of palm oil with methanol. For the purpose of comparison, one standard reaction condition has been selected and was applied for all synthesized catalysts. The reaction parameters are as follows: methanol to oil molar ratio of 15:1, catalysts loading of 3 wt%, reaction temperature of 65 °C and reaction time of 2 hours.

At standard operation condition, the biodiesel conversion of 90.04% was recorded for the modified catalyst ($\text{Ca}(\text{OCH}_3)_2$), while an inferior amount of biodiesel (not calculated) with large soap formation was obtained for the unmodified CaO catalyst. Thus, for the optimization study, only the calcium methoxide catalyst was used to investigate the effect of methanol to oil molar ratio, catalyst loading, and reaction time on the biodiesel conversion.

Figure 5 depicts the effect of methanol to oil molar ratio on the biodiesel conversion catalyzed by calcium methoxide. Since transesterification is an equilibrium reaction, excess of alcohol is required to drive the reaction towards the right. The biodiesel conversion was calculated based on the glycerol produced that has been reported previously [5, 6]. Based on the result, the optimal ratio of methanol to oil molar ratio for transesterification of RCF was 15:1 with a conversion of almost 90.04%. At lower ratio of 5:1, the conversion recorded is less than 50% due to the limited methanol for the reaction to take place. While, at higher ratio of 20:1, the conversion was decreased to 78.50% due to the backward reaction and saturation of the catalytic surface which slower the reaction [14].

The influence of catalyst loading on the biodiesel conversion was depicted in Figure 6. A significant amount of biodiesel (76.92%) was produced even at a low catalyst loading of 1 wt%. The biodiesel increases steadily to 90.04% (3 wt%) and drop slightly when the amount of catalyst was increased up to 4 wt% (87.50%). A study conducted by Gupta et al. [15] on the transesterification of waste cooking oil using calcium diglyceride reported that optimum biodiesel yield (93.5%) was recorded when the catalyst amount used is as low as 1 wt%, while further increment in catalyst loading to 1.25 wt% resulted in a slight decrease in the yield. The drop in the biodiesel conversion was due to the fact that excessive catalyst amount will increase the viscosity of the reaction mixture (catalyst, oil and methanol), which leads to a decrease in yield of methyl ester [16]. Apart from that, when the catalyst amount was too much, more biodiesel products were absorbed by the catalyst that lowering the FAME yield [11] and it will promote the formation of metal soap emulsion [17].

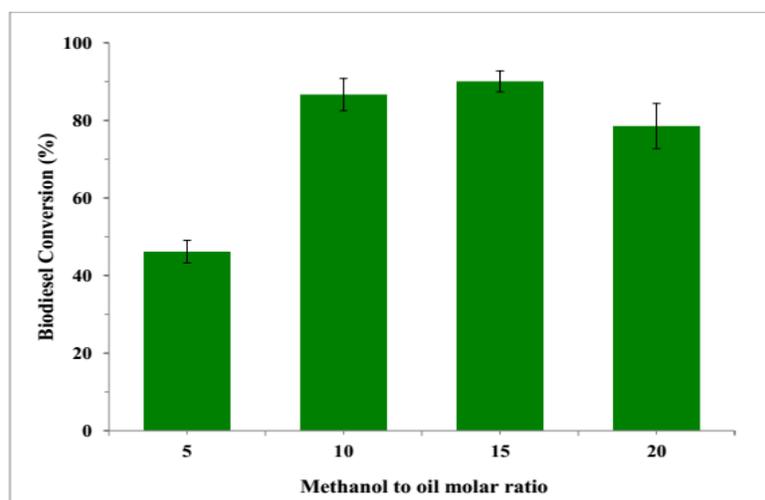


Figure 5. Effect of methanol to oil molar ratio on the biodiesel conversion

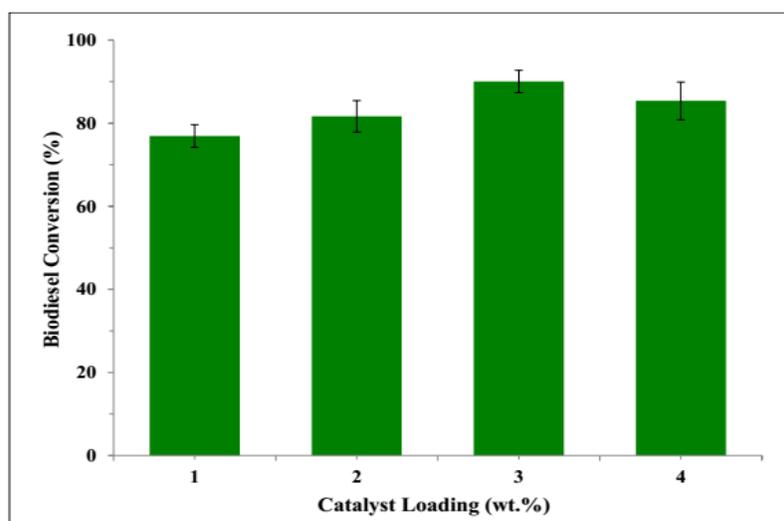


Figure 6. Effect of catalyst loading on the biodiesel conversion

In an economic point of view, effective biodiesel production must be done in a shorter reaction time. However, at the shortest reaction time (30 min), only 11.54% of RCF was converted into biodiesel as shown in [Figure 7](#). As the reaction time increases to 2 h, the conversion was jumped to 90.04%. *Kusuma et al.* [18] reported that the increase in the FAME conversion was obtained when there is sufficient time for the reaction to occur. Nevertheless, when the reaction was prolonged to 3 h, a slight drop of about 16% in the biodiesel conversion was observed. Excess reaction time can influence the FAME yield due to loss of ester as well as soap formation since the transesterification is a reversible reaction [19].

The reusability of the catalyst was carried out based on the optimal reaction parameters as follows; 15:1 methanol to oil molar ratio, 3 wt% catalyst loading and 2 hours reaction time. The

transesterification reaction was conducted at 65 °C and the spent catalyst was reused without any further treatment. [Figure 8](#) shows the repeatable cycle of the catalyst to produce biodiesel under the mentioned condition. The catalyst showed a considerable performance up to 4 consecutive cycles without further washing or calcination steps. One of the reasons for the catalyst deactivation in transesterification reaction is due to the leaching of the active species such as Ca and the adsorption of acidic hydrocarbons onto basic sites [20]. In addition, *Boro et al.* [21] stated that the deactivation could be probably due to the structural changes of the catalyst that lead to the formation of $\text{Ca}(\text{OH})_2$ due to the fact that there is a presence of water in the reactant (RCF and methanol).

The biodiesel produced at each cycle was sent to AAS analysis to confirm the possibility of the leaching of the Ca catalyst into the product. The results show that in all consecutive cycle, the amount of Ca leach out is below the permissible limit (<5 mg/kg), as shown in [Table 2](#).

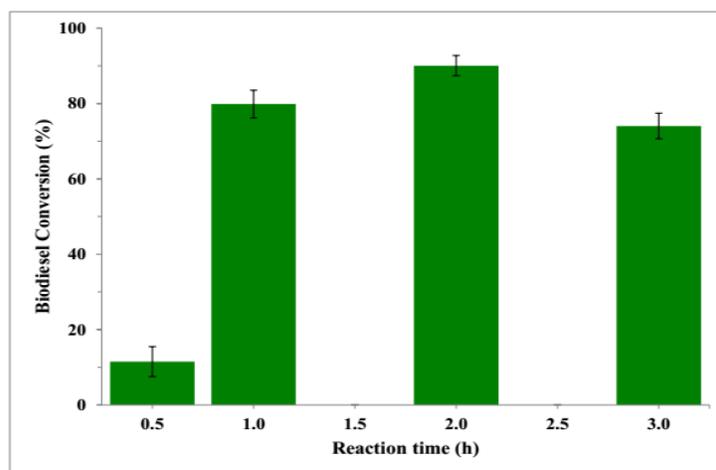


Figure 7. Effect of reaction time on the biodiesel conversion

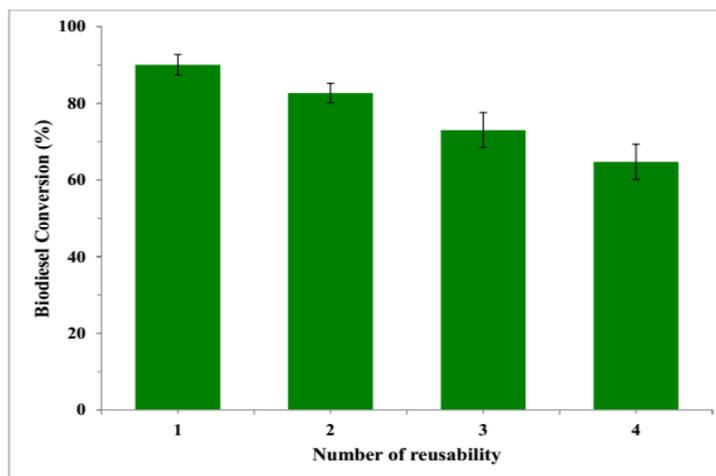


Figure 8. Reusability study of the calcium methoxide catalysts

Table 2. Leaching analysis results of biodiesel using modified CaO catalyst derived from waste chicken eggshells

Cycle of reusability	[Ca] in biodiesel mg/kg	ASTM D6751	EN 14214-2003
1	1.99		
2	1.85	5.00	5.00
3	1.76		

Conclusions

In this study, waste chicken eggshells were utilized as solid basic catalyst in the transesterification of rendered chicken fats into biodiesel. Prior to transesterification reaction, the RCF was undergone esterification reaction to reduce the FFA value to less than 1.0%. The superior catalytic performance of the calcium methoxide catalyst might be attributed to its higher basic strength, high surface area, and smaller crystallite size compared to that of the unmodified CaO catalyst. The highest biodiesel conversion (90.04%) was achieved under the optimal reaction parameters of 15:1 methanol to oil molar ratio, 3 wt% catalyst loading, 2 h reaction time at 65 °C.

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Disclosure Statement

No potential conflict of interest was reported by the authors.

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