Outstanding performance of waste chicken eggshell derived CaO as a green catalyst in biodiesel production: Optimization of calcination conditions

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Abstract

The utilization of conventional catalyst such as sodium hydroxide in biodiesel production possesses several disadvantages as they are difficult to separate from biodiesel products, particularly prone to soap formation and require a multiple neutralization step. For this reason, CaO derived from waste chicken eggshell was explored as an alternative catalyst. Normally, CaO from natural source was synthesized through the calcination process. Thus, this paper aims to identify the optimum condition of calcination process for high biodiesel yield. On the basis of statistical analysis, a central composite design (CCD) was used to optimize the calcination conditions which are calcination temperature and time to achieve high yield of biodiesel. The calcination temperature and time were varied in the range of 600 to 1000 °C and 60 to 300 minutes, respectively. The optimum calcination conditions are 900 °C and 3.5 hours, whereby the most significant factor affecting biodiesel yield was identified as calcination temperature. The result also indicated that the second order model was adequate for both independent variables on the response with R² of 0.9383. The maximum biodiesel yield of 92.81 and 94.72% were obtained by experimental and predicted values, respectively.

1. Introduction

Viable renewable energy source such as biomass has been used in various forms for the supply of energy in wide range of applications where one of these energy products is known as biodiesel. Biodiesel is a green renewable energy which is starting to gain attention by many researchers upon its viability and is widely utilized as an alternative form of energy resource in many countries around the world and has been found to be a very good alternative for petroleum diesel [1]. It is generally produced via transesterification reaction between triglycerides in vegetable oils or animal fats with methanol in the presence of catalyst.

Commonly, homogeneous catalyst such as sodium hydroxide and potassium hydroxide is the most preferred catalyst used in the industrial scale biodiesel production. Although these types of catalysts have high catalytic activity at mild conditions, they are expensive and very difficult to separate from biodiesel product [2]. Therefore, the usage of heterogeneous catalyst has received considerable attention due to their ease of separation, recycling and purification steps [3]. Among the heterogeneous catalysts, calcium oxide (CaO) is a well-known catalyst that has been widely applied in biodiesel production.
Even though the CaO is highly active and can be reused in biodiesel production, it is important to seek for an alternative in reducing the cost of purchasing the catalyst used. This is where the waste chicken eggshell comes into play. Waste chicken eggshell is a food waste that is mainly discarded from food industry and household. The Department of Statistics Malaysia estimated that Malaysians consume 19.1 kg chicken egg per capita, which makes Malaysia as the sixth highest country regarding egg consumption per person. Thus, a large amount of waste eggshell is generated as they are commonly disposed directly in landfill. In recent years, many efforts have been conducted to transform waste eggshell into a value-added product such as adsorbent for wastewater treatment, biocompatible materials in medical surgery and fertilizer for plants as well as catalyst in biodiesel production [4]. Eggshell consists of around 95% calcium carbonate (CaCO₃) that make it a promising candidate as a source of CaO catalyst.

A large number of studies have examined the application of waste eggshell as catalyst in biodiesel production. Chavan et al. [5] produced CaO catalyst by calcining chicken eggshell at 900 ºC for 2.5 hours and employed the catalyst in the transesterification reaction of jatropha oil. The maximum methyl ester yield was found to be around 90%. Later, Tan et al. [6] conducted biodiesel production from waste cooking oil by using CaO catalyst from chicken eggshell, which undergo calcination at 1000 ºC for 4 hours and resulted 94% of biodiesel yield. Fayyazi et al. [7] used calcined chicken eggshell at 900 ºC for 3 hours on sunflower oil for biodiesel production. The yield of biodiesel was reported to be 93% whereas Kirubakaran and Arul [8] observed 90% of methyl ester by using calcination of chicken eggshell at 900 ºC for 4 hours as the catalyst and chicken fat as the feedstock. Meanwhile, Goli and Sahu [9] studied the catalytic activity of CaO in transesterification reaction of soybean oil by varying the calcination temperature of chicken eggshell in the range of 500 to 1100 ºC for 3 hours. They concluded that the optimum calcination temperature for the eggshell to completely decompose the CaCO₃ to CaO was 900 ºC, whereby the biodiesel yield of 93% was achieved. Another research regarding the effect of calcination temperature on the catalyst properties was conducted by Rahman [10], whereby the chicken eggshell was calcined for 4 hours at temperature of 200, 400, 600, 800 and 1000 ºC. The result revealed that the biodiesel yield from E. compressa algal oil increased with increasing the calcination temperature up to 800 ºC and then decreased beyond this temperature.

However, in all these aforementioned works, no investigation is reported involving the effect of calcination time on the catalytic activity of CaO in the transesterification reaction. For this reason, the statistical analysis using Central Composite Design was conducted in this study to optimize the calcination temperature and time in order to achieve high biodiesel yield.

2. Materials and method
2.1. Materials
Waste cooking oil (WCO) as a source of triglyceride was collected from local restaurant while waste chicken eggshells were obtained from bakery shop in Johor, Malaysia. Methanol (AR grade, ≥ 99.5%) was obtained from Sigma-Aldrich corporation.

2.2. Optimization study
The optimization using Central Composite Design (CCD) method of Response Surface Methodology (RSM) was used in this study since it provides better evaluation and comprehensive analysis of the significance of the independent variables compared to single-factor-at-one-time approach. Two variables and one response were used. The variables investigated are calcination temperature and calcination time.

2.2.1. Catalyst preparation.
The preparation of catalyst from waste chicken eggshell first involved the cleaning process using tap water to remove unwanted contaminants. Next, the waste eggshell was dried for 24 hours at temperature of 70 ºC and then crushed using blender to obtain powder form. Calcination process was carried out
using furnace according to designated temperature and time. Based on previous studies, the calcination temperature should be within the range of 600 and 1000 ºC, whereas the acceptable range of calcination time was 60 to 300 minutes.

2.2.2. Transesterification reaction. 
Transesterification reaction was conducted in two-neck round bottom batch reactor connected with reflux condenser. The experimental set-up was then immersed in silicone oil bath. A fixed amount of 40 mL of WCO was first heated up to 65 ºC. Approximately 5 wt% of catalyst was added into the oil along with methanol at 15:1 methanol-oil molar ratio. The mixture was transferred into a separatory funnel to separate biodiesel and glycerol phase as well as the catalyst after 6 hours of reaction. The volume of the biodiesel product, which is the upper layer was then recorded and the biodiesel yield was calculated according to equation (1), where weight of each sample was determined by multiplying the density and the volume.

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\text{Yield of biodiesel(\%) = \frac{\text{Weight of biodiesel(g)}}{\text{Weight of waste cooking oil (g)}} \times 100}
\]  

(1)

2.3. Catalyst characterization
The FTIR analysis was performed using Perkin–Elmer Spectrum One FTIR spectrophotometer with Spectrum v5.02 software. The XRD measurement was carried out by Bruker D8 Advance diffractometer at a wavelength of 0.1541 nm and using Ni-filter Cu-Kα radiation.

3. Results and discussion
3.1. Optimization study
The results of 10 experimental runs are summarized in Table 1.

| Run | Temperature (ºC) | Time (min) | Biodiesel yield (%) |
|-----|------------------|------------|---------------------|
| 1   | 600              | 60         | 37.54               |
| 2   | 600              | 300        | 49.68               |
| 3   | 1000             | 60         | 86.53               |
| 4   | 1000             | 300        | 81.79               |
| 5   | 517              | 180        | 34.69               |
| 6   | 1082             | 180        | 76.98               |
| 7   | 800              | 10         | 56.17               |
| 8   | 800              | 350        | 91.16               |
| 9   | 800              | 180        | 89.38               |
| 10  | 800              | 180        | 89.38               |

The analysis of variance (ANOVA) was performed to determine the quality of model prediction and the result was shown in Table 2.

Table 2. Analysis of variance (ANOVA) for biodiesel yield
The calculated value of $F$-value in Table 2 was found to be 12.25, which was higher than the tabulated value of $F_{0.05}$, and thus indicates that the model is significant. The coefficient of determination ($R^2$) determines whether the model fits the data, whereby 0.9387 was obtained in this study. As a remark, this model suggests a strong correlation between the experimental and predicted values, as shown in Figure 1.

The Pareto Chart is presented in Figure 2, whereby the significance of each independent variable and the interaction between them on the biodiesel yield can be evaluated based on the length of the bars. As shown in Figure 2, the calcination temperature has the most significant effect on the yield of biodiesel. On the other hand, the lower contribution of calcination time in prediction of the biodiesel yield is presented as the reference line remains inside.

For the regression coefficient of independent variables, both the sign and magnitude are important. The direction of the proportionality independent variable on the response was indicated by the sign, whereby the negative sign means that the independent variable is inversely proportional to the response while a positive sign means the opposite. It was found that the linear effect of calcination temperature ($X_1$) and calcination time ($X_2$) exhibited positive relationship with the biodiesel yield. Whereas, the quadratic term of calcination temperature ($X_1^2$) and calcination time ($X_2^2$), along with the interaction effect of both variables ($X_1X_2$) showed negative effect on the yield.

**Figure 1.** The comparison of predicted value against the actual value by the RSM

**Figure 2.** Pareto chart showing the effect of calcination temperature and time as well as their interaction on the biodiesel yield

Figure 3 demonstrates the effect of calcination temperature on the biodiesel yield by interaction with calcination time. The positive effect of calcination temperature was demonstrated as the yield of biodiesel increases with increase in temperature. According to Rahman [10], the catalytic activity of produced catalyst that was calcined below 600 ºC was very low due to the incomplete formation of CaO. However, further increase in calcination temperature may lead to high sintering rate and excessive structure collapse, which resulted in the suppression of catalytic activity. The positive effect can also be
seen in calcination time, whereby the higher conversion from CaCO$_3$ to CaO was occurred with the longer time allows the CaCO$_3$ to proceed toward higher CaO conversion. Nonetheless, a longer calcination time under high temperature also may result in catalyst deactivation due to sintering effect.

![Figure 3. Surface plot of the effect of interaction between calcination temperature and calcination time on biodiesel yield.](image)

Based on the plots of response surface and contour, the optimum of independent variables was found to be at 895.8498 ºC of calcination temperature and 217.8113 minutes of calcination time. At these optimized conditions, the maximum yield of biodiesel was predicted as 94.7208% by the quadratic response surface model. The experiment was repeated three times using the optimized conditions, whereby the calcination temperature and time were set at 896 ºC and 218 minutes, respectively, to verify the modeling results.

The average yield of biodiesel by experiment was found to be 92.81%. The result obtained showed a good correlation between experimental and predicted values and consequently verified the predictive model. As a final remark, it was recommended that the calcination condition is around 900 ºC for 3.5 hours.

3.2. Characterization of catalyst
3.2.1. Fourier transform infrared spectroscopy.
The FTIR spectrum of CaO catalyst prepared under calcination condition of 900 ºC for 3.5 hours is presented in Figure 4.
Figure 4. FTIR spectra of the CaO catalyst

From the FTIR result, the vibration mode of CO$_3^{2-}$ ions resulted from the chemisorption of CO$_2$ on the catalyst surface can be seen at the absorption band of 873, 1082 and 1478 cm$^{-1}$ [11]. A sharp peak obtained at 3639 cm$^{-1}$ can be assigned to the stretching band of OH$^-$ in Ca(OH)$_2$ that was formed during the adsorption of water from the atmosphere on the CaO surface [6,12]. Meanwhile, the absorption band at 854 cm$^{-1}$ was attributed to the stretching mode of C-O bond on the catalyst surface [13]. The strong peak at 528 cm$^{-1}$ was associated with the stretching vibration of the Ca-O bond [14], which is indicative of the successful formation of calcium oxide during the calcination process of waste chicken eggshell.

3.2.2. X-ray diffraction.

The XRD result supports the findings in the FTIR, which is illustrated in Figure 5.

Figure 5. XRD pattern of the CaO catalyst

As shown in Figure 5, the diffraction peaks at 20 of 18.1, 32.3, 37.5, 54.0, 64.3, 67.5 and 88.6$^\circ$ were corresponding to CaO phase [2], thus confirm the transformation of CaCO$_3$ into CaO that could act as a highly active catalyst in transesterification reaction. The presence of minor amount of CaCO$_3$ can also be observed as a very low intensity peak at 34.2 and 50.9$^\circ$, whereas the characteristic peak for Ca(OH)$_2$ appeared at 47.3$^\circ$ [15].
4. Conclusion
In this study, CaO catalyst was successfully produced from waste chicken eggshell through calcination process as confirmed by FTIR and XRD results. From optimization study via RSM method, it has been demonstrated that the calcination temperature is the most significant variable that influence the yield of biodiesel. The results of the optimization imply that the calcination process conducted at 900 ºC for 3.5 hours provide the maximum value of biodiesel yield. The predicted values by the model is in good agreement with the experimental values indicating that the model can be used to optimize the production of CaO catalyst via calcination process.

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