Optimally Efficient Biodiesel Conversion From Used Cooking Oil by Zeolite Supported Calcium Oxide Catalyst
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ABSTRACT
Biodiesel is conventionally catalyzed by homogeneous catalyst such as sodium hydroxide or potassium hydroxide, which possesses several disadvantages as they are difficult to separate from biodiesel products and require a multiple neutralization step. Therefore, the usage and development of heterogeneous catalyst has attracted the most research attention over the last few years to overcome those issues. In this study, zeolite supported calcium oxide (CaO) was synthesized and then characterized using Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) analysis. Subsequently, their performance as catalyst was tested by carrying out the transesterification reaction of used cooking oil (UCO). A focus of this paper is to determine the optimum reaction conditions and evaluate their effect on the yield of biodiesel. The FTIR and XRD results of the supported catalyst confirmed the presence of both CaO and zeolite components. The optimum conditions, which gave biodiesel yield of 86.82%, were recorded to be a 3 wt% catalyst concentration, 15:1 methanol to oil molar ratio, 65 °C reaction temperature and 1 h reaction time.

Keywords: Biodiesel, calcium oxide, zeolite, used cooking oil, heterogeneous catalyst

1. INTRODUCTION
The application of biodiesel as a transportation fuel has been highlighted by many researchers in the last few years. As far as environmental sustainability is concerned, biodiesel shows numerous advantages compared to fossil fuels such as non-toxic, biodegradable, possesses inherent lubricity, high flash point and emits low greenhouse gas emissions [1, 2, 3].

Chemically, biodiesel is composed of long-chain fatty acid alkyl esters which are synthesized from a reaction between triglycerides in vegetable oils or animal fats with an alcohol in the presence of catalyst, namely transesterification reaction [4, 5]. The catalyst used in the transesterification reaction could be either homogeneous or heterogeneous catalyst. Both catalysts offer a number of advantages that has made them beneficial in their own way. However, the major drawback of homogeneous catalyst is that they cannot be reused, which make the heterogeneous catalysts are of great interest in the field of catalysis.

Among the different types of heterogeneous catalyst available, CaO supported with high surface area material such as zeolite can be seen to have the potential as an active catalyst in the transesterification reaction. At present, there have been only a small number of researches focusing on the use of CaO/zeolite catalyst in biodiesel production. Wu et al. [6] studied commercial CaO supported with Na-Y zeolite as catalyst in the transesterification reaction of soybean oil, obtaining of biodiesel yield of 95% with catalyst loading of 3 wt% and methanol to oil molar ratio of 9:1 at 65 °C for 3 h. Later, Purnamasari et al. [7] has reported the synthesis of CaO/zeolite by impregnating calcium acetate on the ZSM-5 zeolite followed by calcination at 800 °C for 2 h. The catalytic activity of the prepared catalyst was examined in the transesterification of used cooking oil and the biodiesel yield was recorded to be 29.73% at reaction conditions of 2 wt% amount of catalyst, 12:1 methanol to oil molar ratio, 65 °C reaction temperature and 2 h reaction time. Using the same CaO source of calcium acetate, Lawan et al. [8] studied the optimization of biodiesel from waste lard catalyzed by CaO/ZSM-5 zeolite under microwave irradiation using response surface methodology (RSM) based central composite design (CCD) approach. The optimal reaction conditions were found to be 8 wt/vol catalyst loading, 30:1 methanol to oil molar ratio, 1.25 h reaction time and 595 Watts microwave power, which has led to yield of 90.89%. In this work, an active heterogeneous catalyst based on CaO/zeolite was developed for the transesterification reaction of UCO. The waste chicken eggshell, that is one of the typical wastes from Malaysia food industry and household, was employed as a source material of the CaO. Prior transesterification reaction, the chicken eggshells materials was initially calcined at 900 °C for 3 h then impregnated with commercial ZSM-5 zeolite and recalcined. The catalytic activity of the prepared catalyst was studied in a batch reactor by varying the reaction
parameters, which are the catalyst dosage (3–13 wt%), methanol to oil molar ratio (5:1–20:1), the reaction time (1–4 h) and reaction temperature (30–100 °C). It was noteworthy to mention that there were no proceeding reports in the open literature on the usage of CaO derived from waste chicken eggshell in the preparation of CaO/zeolite catalyst. Hence, this was done for the first time in this work and the use of this waste materials gives a value-added to the catalyst production.

2. EXPERIMENTAL

2.1. Materials

The raw materials involved in the study are waste chicken eggshell and used cooking oil (UCO), whereby both of these materials were collected at local restaurant in Universiti Teknologi Malaysia. Other chemicals used were of analytical grade and are listed as follows: ZSM-5 zeolite (Acros Organics, 400 to 570 molar ratio SiO2/Al2O3) and methanol (Qrec, 99.8%).

2.2. Synthesis of CaO/zeolite Catalyst

Firstly, waste chicken eggshell was washed thoroughly with tap water several times to remove impurities followed by drying in oven at 80 °C overnight and grinding to produce a fine-sized powder. The eggshell powder was then calcined in furnace at 900 °C for 3 h to transform CaCO3 to CaO catalyst. Subsequently, approximately 1.5 g of obtained CaO was mixed with 100 mL of distilled water at 80 °C under reflux with continuous stirring. After 30 mins, about 5 g of ZSM-5 zeolite was added and the solution was kept stirring for 4 h at 80 °C. The solution was then filtered and the residue was dried in oven at 80 °C overnight. Lastly, the dried powdered was calcined in furnace at 900 °C for 3 h.

2.3. Characterization of CaO/zeolite Catalyst

The X-ray diffraction (XRD) patterns of catalyst in the 20 range of 3 to 70° was obtained using Bruker D8 Advance diffractometer with Cu Kα radiation (λ = 0.1541 nm) at 40 kV and 40 mA. Meanwhile, the Fourier transform infrared spectroscopy (FTIR) spectra of catalyst was recorded on Perkin-Elmer Spectrum One FTIR Spectrometer by employing the conventional KBr disk method.

2.4. Biodiesel Production

Initially, about 20 mL of UCO was placed in round bottom flask equipped with reflux condenser and thermometer. This apparatus was then immersed in silicone oil bath and was heated at certain temperature (30, 45, 65 and 100 °C). Subsequently, a designated amount of catalyst (3, 7, 10 and 13 wt% catalyst with respect to weight of UCO) and methanol (5:1, 10:1, 15:1 and 20:1 methanol to oil molar ratio) were added into the flask, and the mixture was continuously stirred for different time (1, 2, 3 and 4 h). After completion, the catalyst was removed by filtration. The filtrate was transferred into separatory funnel and left overnight. Two layers were then obtained, whereby the upper layer is biodiesel and lower layer is glycerol. The biodiesel phase was collected and weighted. The yield of biodiesel was determined according to Eq. (1).

\[
\text{Biodiesel yield} \% = \left( \frac{W_W}{W_W} \right) \times 100 \%
\]

Where \(W_W\) is the weight of UCO and \(W_0\) is the weight of biodiesel.

3. RESULTS AND DISCUSSION

3.1. Characterization of CaO/zeolite Catalyst

Figure 1 shows the XRD pattern of CaO/zeolite catalyst. The diffraction peak of ZSM-5 zeolite was identified at 20 of 7.95, 8.86, 14.84, 20.96, 21.82, 23.16, 24 and 24.54° in accordance to JCPDS file no. 01-070-4743. The appearance of these peaks was found to be similar to those reported by Wen et al. [9] and Zhokh et al. [10]. Meanwhile, the peaks at 20 of 11.54, 17.88, 26.94, 28.92, 29.98, 36.26, 38.3, 41.24, 45.24, 49.68, 52.06 and 57.34° were corresponded to calcium silicate (JCPDS file no. 00-042-0547), which indicates the successful impregnation of CaO with silica in zeolite structures. A significant peak of calcium silicate at 20 of 29.98° in this study matched the reported result from Ganesan et al. [11]. The FTIR spectra of the zeolite supported CaO catalyst is shown in Figure 2. From the FTIR result, the stretching vibration of hydroxyl group can be seen at the absorption band of 3650 cm\(^{-1}\), which eventually adsorbed water on the catalyst surface as well as Al-OH and Si-OH groups from zeolite [12, 13]. The presence of CaO was indicated by the peaks around 2377 and 899 cm\(^{-1}\) correspond to the stretching vibrations of C–H and C–O bonds, respectively [7]. Meanwhile, the absorption bands obtained at 1078 and 797 cm\(^{-1}\) were respectively associated to the asymmetric and symmetric stretching vibration of Si–O–Si bonds in the
zeolite structure [14, 15]. The five-member ring structure of ZSM-5 zeolite was reflected by peaks appearing at 562 cm$^{-1}$ [16] and the peaks at 457 cm$^{-1}$ arises was due to the internal tetrahedral TO4 (T= Si, Al) [14]. These findings confirmed the existence of CaO and zeolite components, which was further verified the successful production of CaO/zeolite catalyst.

The effect of methanol to oil molar ratio on biodiesel yield is studied by varying the ratio from 5:1 to 20:1 and maintaining the catalyst dosage at 10 wt% with reaction temperature of 65 °C and time of 1 h. The result is presented in Figure 4. Biodiesel yield is increased from 73.07 to 80.57% with increase in methanol to oil molar ratio from 5:1 to 10:1. An increment of biodiesel yield in higher amount of methanol most probably due to formation of more methoxide active species that promote transesterification in the forward direction and thereby increased the reaction rate [19, 20]. However, the biodiesel yield was started to decrease to 79.66 and 72.5% beyond 10:1 methanol to oil molar ratio. According to Farooq and Ramli [21], an equilibrium shifts in the reverse direction is likely to be happened when the produced glycerol during reaction is largely dissolve in the excessive methanol, which in turn results in low biodiesel yield.

3.2. Effect of Reaction Conditions on Biodiesel Production

Figure 3 depicts the effect of catalyst dosage on biodiesel yield. The dosage of catalyst was varied from 3 to 13 wt%, while a fixed amount of 15:1 of methanol to oil molar ratio was used at 65 °C reaction temperature for 1 h reaction time. It is observed that the biodiesel yield decreases slowly from 86.82% at 3 wt% to 82.33 and 79.66% when the catalyst was added at 7 and 10 wt%, respectively. Subsequently, a significant reduction of yield from 79.66 to 66.48% was observed with further addition of 13 wt% catalyst. The lower biodiesel yield with higher catalyst dosage could be related to the formation of slurry, which tends to make the reaction system to be more viscous and hence limiting their mass transfer capacities [17, 18]. Therefore, the dosage of CaO/zeolite catalyst as low as 3 wt% is sufficient to achieve high biodiesel yield.

The reaction time, ranging from 1 to 4 h, was investigated to evaluate the effect of time on biodiesel yield as shown in Figure 5. The transesterification reaction was carried out at constant temperature of 65 °C by using 10 wt% catalyst dosage and 15:1 methanol to oil molar ratio. The reaction time appears to have no significant effect, whereby the biodiesel yield of 79.66, 77.56, 76.08 and 78.86% was recorded at reaction time of 1, 2, 3 and 4 h, respectively. This trend could be explained due to the fact that the reaction reach in an equilibrium condition and no further reaction takes place, as reported by Kirubakaran and Arul Mozhi Selvan [17] and Rahman [22].
Figure 6 shows biodiesel yield when reaction temperature was varied from 30 to 100 °C. Herein, the transesterification reaction was performed for 1 h with catalyst dosage of 10 wt% and methanol to oil molar ratio of 15:1. The experimental results indicated that the biodiesel yield increased as the reaction temperature was increased and the optimum yield of 79.66% was obtained at 65 °C. A slight decrease in biodiesel yield was observed beyond the optimum temperature, which is associated to the evaporation of methanol as their boiling point is 65 °C [23].

![Figure 6](image_url) Effect of reaction temperature on biodiesel yield

4. CONCLUSION

Present work has shown the optimum reaction conditions for the production of biodiesel from UCO catalyzed by zeolite supported CaO. The maximum biodiesel yield of 86.62% was achieved when the catalyst amount was 3 wt%, the methanol to oil molar ratio was 15:1 and the reaction temperature was 65 °C with 1 h reaction time. Herein, these optimum conditions can be used in large-scale production to reduce the biodiesel production cost. Furthermore, CaO/zeolite presents great potential as efficient green catalyst in the biodiesel production from low-cost UCO.

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