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Pilot Evaluation of Calcium Titanate Catalyst for Biodiesel Production from Waste Cooking Oil

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The world is gradually moving toward a severe energy crisis due to depletion of fossil fuels. Biodiesel is one of the technically and economically feasible options to solve the aforesaid problem. However, the overall costs of biodiesel production associated with the increasing market price of its feedstock clearly influence the profitability of the process. Therefore, biodiesel production has been directed toward waste materials as feedstock such as waste cooking oil (WCO). On the other hands, WCO is dealing with high free fatty acids (FFA) contents which gives a significant effect to the transesterification reaction, resulting in a lower biodiesel production. Therefore, a viable catalyst is needed for wide industrial usage in biodiesel synthesis from WCO. CaO is one of the promising heterogeneous catalyst for the transesterification reaction. However, CaO is deals with some limitations that need to overcome. This research paper deals with the synthesis of heterogeneous calcium titanate (CT) catalyst from calcium oxide (CaO) and titanium precursor by a sol-gel method for pilot evaluation in biodiesel production. CT catalyst was produced under different calcination temperature (200 °C, 400 °C, 600 °C, 800 °C). The synthesized catalysts were evaluated for performance in transesterification reaction of methanol with WCO. BET surface area, XRD, and SEM were measured to correlate the activity with the structural features of the catalysts. The results exhibited that the calcination temperature of 400 °C is more preferable in terms of technical and economic feasibility. A biodiesel yield of 80.0 % was observed with a methanol to oil molar ratio of 15:1 and 1 wt. % of CT catalyst loading amount in 1 h at 65 °C which is comparative with commercial CaO catalyst calcined at 400 °C (60.0 % of biodiesel yield) at the same reaction conditions.

1. Introduction

The production of biodiesel from waste cooking oil (WCO) has attracted increasing attention in recent years (Doğan, 2016). The transesterification reaction is one of the best known mechanisms for producing biodiesel from WCO. Majority of biodiesel production is based on homogeneous catalytic systems using bases like NaOH and KOH. Although these catalysts are highly active, it is not possible to recover the used alkali and the product needs to be purified, which leads to large amounts of wastewater (Martins et al., 2013). In contrast, heterogeneous catalysts can be recovered after the reaction and reused several times, which in turn produces less wastewater (Kaur and Ali, 2015). These benefits have increased the interest in the development of a heterogeneous catalyst for biodiesel production.

The current literature reports about various new solid basic catalysts for the heterogeneous transesterification to biodiesel (Nasreen et al., 2015). From the literature, it shows that the most common alkaline metal found on those catalysts are calcium oxide (CaO). CaO is a potential one for its low cost, high basic strength and low methanol solubility (Yin et al., 2016). While the relatively low surface area of CaO baffles its application to disperse its active sites to a large molecule of reactants (Asikin-mijan et al., 2015). Many works have been devoted to increase the surface area of CaO catalyst. One of the favourable work is incorporating CaO onto another metal oxide carrier. Recently, calcium-based mixed metal oxide catalysts have attracted an increased amount of attention due to their tunable surface area through alteration of their chemical composition and synthesis procedure.

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By addressing on this, an attempt has been made in the present work to convert WCO to form biodiesel by using calcium titanate (CT) catalyst. This study was focused on investigating the versatility of the catalyst by the incorporation of calcium in order to improve their limitations to have good performance in the transesterification reaction. Titanium was chosen for this research because it possessed a vital support criterion for accelerating heterogeneous catalysed transesterification.

In this research, the preparation of catalyst using the way of the sol-gel method was reported. Further study on the role of the calcination temperature on the structural and morphological of the catalyst, and how those properties contributes to the catalytic activity were included. The as-synthesized catalysts were characterized by using the Brunauer-Emmer-Teller (BET) surface area, X-ray diffraction (XRD), and scanning electron microscopy (SEM) methods.

2. Materials and methods

2.1 Material and chemicals

WCO was collected from the university's cafeteria. WCO was filtered to remove impurities prior to the reaction. The properties of WCO used in this work were identified and are tabulated in Table 1. Titanium tetrabutoxide, $Ti(OCH_2CH_2CH_2CH_3)_4$ (Sigma Aldrich, 97.0 %), Calcium hydroxide, $Ca(OH)_2$ (QRec, 99.0 %), Butanol, C_4H_9OH (ORec, 99.0 %), Methanol, CH_5OH (QRec, 99.0 %), n-Heptane, C_7H_{16} (Merck, 99.0 %) were purchased and used for transesterification reactions and for the analysis of fatty acid methyl esters (FAMEs) evaluation. Analytical reagent grades were applied throughout the experimental. Those chemicals were used without further purification.

Table 1: Chemical and physical properties of WCO

Properties	Value
Free fatty acid (FFA) composition (%)	
Palmitic (C16:0)	34.80
Stearic (C18:0)	7.90
Oleic (C18:1)	53.30
Linoleic (C18:2)	4.00
Density (g/cm^3)	0.91
Acid value (mg KOH/g)	3.75
Saponification value (mg KOH/g)	194.40
Water content (%)	0.20
Calorific value (MJ/kg)	38.62

2.2 Catalyst preparation

In brief, CT was synthesized by a sol-gel method based on Marciniuk et al. (2014), in which $Ca(OH)_2$ and $Ti(OCH_2CH_2CH_2CH_3)_4$ were used as a precursor of calcium and titanate. Firstly, 0.75 ml of $Ti(OCH_2CH_2CH_2CH_3)_4$ was dissolved in 50 ml of C_4H_9OH. In a separate beaker, 1.6 g of $Ca(OH)_2$ was dissolved in 100 mL of water. Both solutions were heated to 55 °C. Then, those solutions were mixed and continue to heat to 55 °C. Then, the mixture was added simultaneously to 230 mL of water and then heated to 55 °C followed by agitation for 40 min. The precipitate formed was subsequently dried at 60 °C for 24 h prior to the calcination step (200, 400, 600, 800 °C) for 2 h in a muffle furnace. After completion, the calcined catalysts were kept in a sample bottle and stored in desiccators.

2.3 Catalyst characterization

The total surface area of the catalysts was carried out using the BET method using a Micromeritics 3 Flex surface characterization analyzer.

The powder XRD analysis was carried out using a PANAlytical X'Pert diffractomer, using Cu Kα radiation (40 kV and 100 mA) with a wavelength of 1.54178 Å, over a 2θ range from 10° to 80° with a step of 0.02° at a screening speed of 10 s.

The surface structure was observed with a JSM-6390LV (JEOL) SEM spectroscopic at room temperature. An accelerating voltage of 10 kV was used to conduct the analysis. All samples were coated with platinum before the analysis.

2.4 Catalytic Test

Typically, transesterification reactions were carried out in a glass-made reaction flask (250 mL) equipped with a reflux condenser, a thermometer and a hot plate with a magnetic stirrer. Then, 30 mL of WCO, methanol to oil molar ratio of 15:1, catalyst loading amount of 1 wt. %, and reaction time of 1 h were used. The mixture was refluxed at fixed temperature of 65 °C with vigorous stirring in a silicone oil bath. Then, the heating was stopped and the flask was left to cool down to room temperature. After the reaction completion, the used catalysts were separated from the reaction medium by filtration and the biodiesel yield was calculated using Eq(1) (Ho et al. 2014).

$$\text{Biodiesel yield (\%)} = \frac{\text{Amount of biodiesel (g)}}{\text{Amount of WCO (g)}} \times 100\ \% \qquad (1)$$

2.5 Product analysis

Gas chromatography-mass spectrometry (GC-MS), model Agilent Technologies 6890N with an inert mass selective detector 5975 has been used to evaluate the composition compound of produced biodiesel (Mohd Ali et al., 2015). Agilent 19091S-433 HP-5MS (30 mm x 250 µm x 0.25 µm), with Helium (He) as the carrier gas has been used. The oven temperature of GC was held at an initial temperature of 120 °C for 0.5 min and then ramped to a final temperature of 300 °C at a rate of 10 °C/min, held for 5 min. The injector and detector temperature was 250 °C while He gas was flow at 1.5 mL/min.

3. Results and discussion

3.1 Catalyst characterization

Table 2 records the surface areas of the CT catalysts after calcination at 200, 400, 600 and 800 °C. The trend of the surface areas is uneven which is not directly proportional to the calcination temperature. Initially, CT catalyst calcined at 200 °C shows the highest surface area about 72.34 m^2/g. The surface area decreased tremendously to 18.45 m^2/g after calcination at 400 °C. The surface area was continuously decreased slightly towards 600 °C of the calcination temperature. At 800 °C, the surface area of CT catalyst was about to increase. The uneven trend may be attributed to the loss of structural phase caused by the phase transformation of the compounds.

Table 2: BET surface area of CT catalysts at different calcination temperature

Calcination temperature (°C)	S_{BET} (m^2/g)
200	72.34
400	18.45
600	17.15
800	41.06

Figure 1 shows the XRD pattern of CT catalyst at a calcination temperature of 200, 400, 600 and 800 °C. Generally, the figure shows the sharp peaks appeared similarly for all calcination temperatures at 2θ = 29.4º, 39.5°, 43.2°, and 48.5°. All those peaks referred to $CaCO_3$ (calcite) and TiO_2 (anatase) phase. For those XRD patterns, a new peak which at 2θ = 57.5° for the new phase of the samples containing calcium and titanium elements also appeared. This new phase indicates the incorporation of Ca^{2+} ions from $Ca(OH)_2$ onto the vacancies in the structure of titanium with hydroxyl groups to form Ti-O-Ca on the surface during calcination step. Another peak that corresponds to the $CaTiO_3$ phase also can be seen at 2θ = 33.2°. However, this peak was only arose for calcination temperature of 600 and 800 °C which indicate that the phase comprises of rutile phase of TiO_2 since at temperature higher than 550 °C, the anatase phase transform to rutile phase. The minor reflection peaks of 18° and 34.1° for 2θ at calcination temperature 200 °C indicate the peaks for $Ca(OH)_2$ phases. These peaks did not appear at a calcination temperature of 400, 600 and 800 °C. This shows that, the original peaks of $Ca(OH)_2$ disappeared above the calcination temperature of 200 °C.

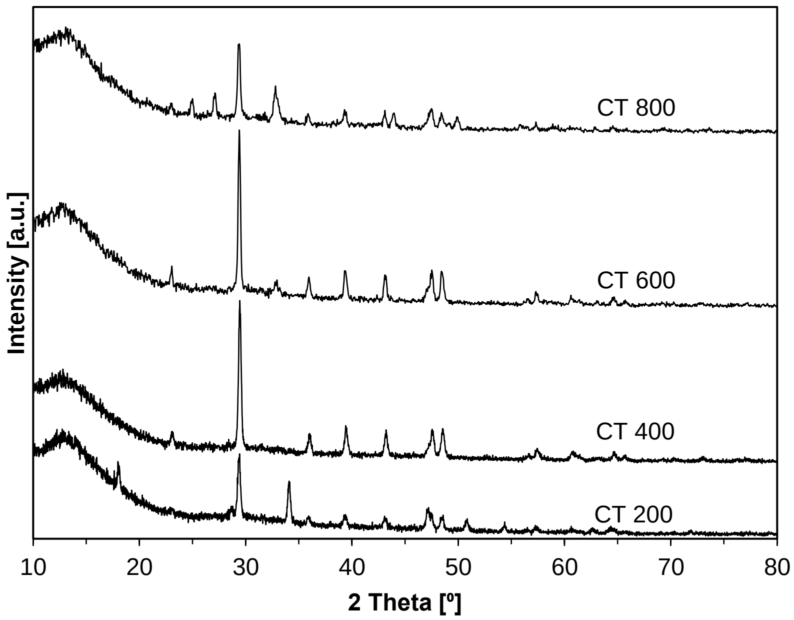

Figure 1: XRD patterns of calcium titanate (CT) catalysts at various calcination temperature (200, 400, 600, 800 °C)

To observe the morphology changes of the calcined catalysts, scanning electron micrographs of all CT catalysts were recorded in Figure 2. It is clearly shown that the micrographs of CT catalysts had a dense surface with a heterogeneous distribution of particle sizes (irregular size). The surface morphologies of the catalyst will directly affect the productivity of biodiesel. This is because the triglyceride molecules would react with methanol molecules on the active sites of the catalyst. Since the catalysts show uneven surface, therefore it suggests that the reaction happens inside and outside the surface of the catalyst. The morphology of the CT catalysts however did not show any significant alterations and always consisted of agglomerates. These findings suggest a good dispersion of Ca species on the Ti surface at different calcination temperature. Besides that, it shows that the structure of the catalyst was retained even in the increase of calcination temperature. From both surface area and XRD pattern characterization results, calcination temperature of 400 °C is more preferable in terms of technical and economic feasibility.

3.2 Catalyst performance

The catalytic activity performance results are depicted in Figure 3. In most catalytic transesterification reactions using heterogeneous catalyst, catalyst with the high surface area are preferred to achieve a high percentage of biodiesel yield. However in this study, the most active catalyst shows at among the lower surface area. The surface area obtained from this study still suggest a good dispersion of active site of Ca^{2+} since the biodiesel yield is higher. This is in line with the result analyzed by SEM. From the present study, it seems that 400 °C of calcination temperature is sufficient to achieve higher catalytic activity in 1 h of reaction. It seems that this calcination temperature is contributing to the presence of highly active Ti-O-Ca sites. In addition, the contents of FAME compounds in the highest biodiesel yield were justified through the gas chromatogram as shown in Table 3. The major methyl ester contains in the product was methyl oleate.

A comparative study on transesterification of WCO was also carried out with commercial CaO catalyst under the optimized conditions of CT catalyst to check the feasibility of the catalyst in the present work. The result shows that commercial CaO achieved 60.0 % of biodiesel yield. The highest activity of CT catalyst as compare to commercial CaO catalyst may be due to the improvement of its characteristics. Table 4 shows the comparison of the percentage of biodiesel yield of commercial CaO and CT catalyst in this present study. This study reveals the advantage of CT as heterogeneous catalyst over the commercial CaO catalyst for transesterification of WCO.

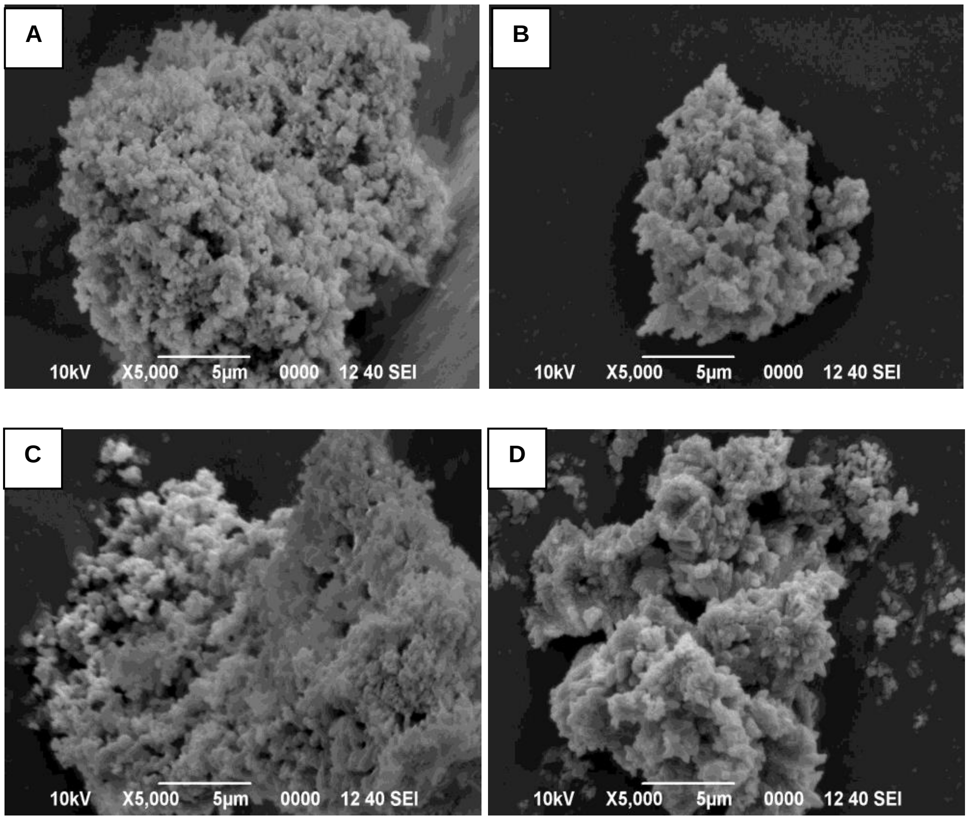

Figure 2: SEM of CT catalysts at various calcination temperature (A) 200 °C, (B) 400 °C, (C) 600 °C and (D) 800 °C

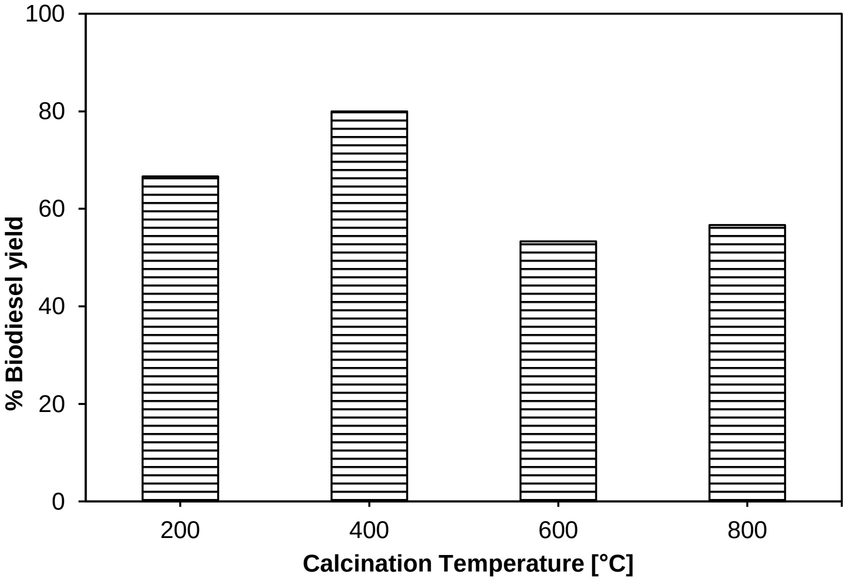

Figure 3: Percentage of biodiesel yield versus calcination temperature for CT catalyst calcined at various calcination temperature

Table 3: FAME compositions in the product

Fatty acid methyl esters (FAME)	Value (%)
Palmitic (C16:0)	32.75
Stearic (C18:0)	8.48
Oleic (C18:1)	42.21
Linoleic (C18:2)	16.56

Table 4: Comparison of percentage of biodiesel yield of CT catalyst with commercial CaO catalyst

Catalyst	Biodiesel yield (%)
CT	80.0
CaO	60.0

4. Conclusion

The CT catalyst synthesized by sol-gel method was found to be potential for the production of biodiesel from WCO. The CT catalyst requires a moderate surface area to be highly active. XRD characterization of the catalysts confirmed the apparent of the peaks that contribute to the active phase of the catalyst. The surface morphology of the catalyst was retained even after the increment of the calcination temperature. In this study, about 80.0 % of biodiesel yield was obtained which is higher than commercial CaO calcined at the same calcination temperature with the same reaction conditions. The FAME peaks obtained from GCMS analysis confirmed the formation of biodiesel production.

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