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Transesterification of waste cooking palm oil and palm oil to fatty acid methyl ester using cesium-modified silica catalyst

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ABSTRACT

The transesterification of waste cooking palm oil (WCPO) and palm oil (PO) with methanol to fatty acid methyl ester (FAME) was studied using CsM-SiO_2 as a heterogeneous catalyst. The catalyst was prepared by an impregnation method with 10%–30% CsO_2 loaded onto silica. The catalyst with 25% loading achieved the highest FAME content. The effects of catalyst on transesterification reaction parameters to FAME content were investigated. The FAME content reached 90% at 65 °C in 3 h with 3 wt.% catalyst loading and 20:1 molar ratio of methanol to oil for WCPO transesterification and 89% with 2 wt.% catalysts loading for PO transesterification, respectively. The solid catalyst can be reused for four batch cycles without significant deactivation. Also, the catalyst exhibited good tolerance toward 1 wt. % water content in WCPO feedstock, without significant changes in the FAME content.

1. Introduction

Biodiesel consisting of a mixture of fatty acid alkyl esters (FAAEs) are non-toxic, ecofriendly, and renewable fuels that are promising alternative to conventional fossil fuels [1,2]. The most reported method of producing biodiesel is the transesterification of vegetable oils and animal fats with methanol in the presence of an acid or basic catalyst [3]. Base catalysts are usually preferred over acid catalysts because of the higher reaction rate and lower reaction temperature than those required in an acid catalyst system [4].Generally, most industrial applications use homogeneous base catalysts such as NaOH or KOH [5]. The separation of catalyst and by-products from the esters is difficult and results in high amounts of wasted water and energy. Hence, heterogeneous base catalysts such as MgO, NaOH, CaO, KOH, and MgO-CeO_2 have been studied for biodiesel production [6–8]. The use of silica support catalysts has also been explored.

The silica supported catalyst generally receives significant attention as solid catalysts for various reactions. The silica modified with alkaline metal oxides is a potential catalyst due to distinctive features such as considerable diameter pores and workable three-dimensional pore structure [9]. The basic structures for silica catalysts are arranged in a form which is large enough to accommodate spheres with 1.2 nm diameter. Among the all silica catalysts used, raw silica is the most widely employed materials [10]. Hossein Kazemian et al. used SBA-15 impregnated with cesium as catalyst for the transesterification of canola oil with low yield (25.35%) at a high methanol: oil molar ratio (40:1) and temperature (135 °C) [11].

To make heterogeneously catalyzed biodiesel production economically viable, catalysts are required to be highly active for diverse classes of triglycerides, operate at near-ambient conditions with low methanol:oil ratios, and be reusable [8,12,13]. Furthermore, feedstock directly affects quality and cost, so lower-cost feedstock from non-edible or waste oils are required for biodiesel production [14–16]. Transesterification of bitter almond oil, which is not a common source of biodiesel feedstock was reported [17]. Also, activity of Zr-SBA-15 as an acid catalyst for biodiesel production from crude palm oil at a high reaction temperature (200 °C) using 10 wt.% catalyst loading was studied and 70% FAME yield reported [18]. Mostly, the low temperature transesterification reaction is catalyzed by basic catalyst. Therefore, the incorporation of alkaline active component into silica type support might be helpful for transesterification process. Hence, for increasing the basic strength of silica material, first group elements in the periodic table are the best choice as active component, cesium is one of the attractive due to high value of alkalinity. Therefore, cesium supported on raw silica has been used in the transesterification of vegetable oils under conventional reaction conditions process.

In the present study, in order to investigate the role of cesium on silica as heterogeneous catalyst in transesterification of waste cooking palm oil (WCPO) and palm oil (PO), different amount of cesium loading were chosen. In this respect, catalysts with cesium loadings of 10%, 15%, 20%, 25% and 30% were synthesized, characterized and

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tested in the transesterification reaction to choose the most effective cesium loading. A simple and efficient method was used for preparing the catalyst, and transesterification reactions were carried out at ambient temperature. The effects of process parameters such as catalyst amount, alcohol-to-oil molar ratio, reaction time of transesterification reaction, and Cs:SiO_2 ratio on the process were investigated to determine the highest conversion that can be achieved. Also, the reusability and water tolerance of synthesized catalyst were tested.

2. Materials and methods

2.1. Materials

Silica powder (average particle size, 6.66 μm; purity, 99.076% SiO_2) was obtained from local supplier Sibel Co. (Malaysia). Cesium carbonate (Cs_2Co_3, 99%) used to prepare the catalyst was purchase from Sigma–Aldrich Co. (Malaysia). The waste cooking oil was collected from a cafeteria in the Engineering Campus of the University Science Malaysia and properties reported [19]. Raw WCO was treated by simple filtration to remove suspended solids and then heated at 110 °C for 2 h to remove all moisture. HPLC grade methanol used for the transesterification reactions was purchased from Merck Co. (Malaysia).

2.2. Catalyst preparation

To prepare Cs-doped silica supported catalysts, a desired amount of $CsCO_3$ need to be dissolved in a mixture of 50:50 (v/v) deionized water and ethanol. Different Cs loading levels were prepared on silica, *i.e*., 10%–30% (w/w) and hereafter denoted as CsM-SiO_2 (M: cesium weight percentage).

Impregnation was performed by facilitating contact between the support and solution (4 mL/g support) for 24 h under constant stirring. Then, the excess solution was removed with a rotary evaporator, and the catalyst was subsequently washed excessively with deionized water followed by drying at 110 °C for 2 h. The dry catalyst was calcined between the 250 °C and 450 °C in air for 4 h. Then, 300 °C is the optimal calcination temperature used in the subsequent experimental runs. Similarly, Cs_2O and SiO_2 catalysts were prepared under the same treatment conditions. Then activity of individual Cs_2O and SiO_2 catalysts were tested to compare the effect of element combination during WCPO transesterification reaction.

2.3. Catalyst characterization

The chemical and physical properties of the synthesized catalysts (Cs-SiO_2) were investigated by using different characterization techniques. The synthesized catalysts in their various categories were subjected to analysis and characterized techniques such as nitrogen adsorption–desorption technique, powder X-ray diffraction (XRD), energy dispersive X-ray (EDX), surface scanning electron microscopy (SEM), Fourier transform infrared (FTIR), Hammet indicators (H_) for basic strengths in a specific range of materials and transmission electron microscopy (HRTEM) was also done for selected catalyst preparation to obtain further insights into the catalysts microstructure. The nitrogen adsorption–desorption isotherms for the synthesized catalysts were measured by ASAP 2020 V3.02 H Micromeritics surface area and porosity analyser at 77 K. The analysis was done to obtain the surface area, pore size distribution and pore volume of the synthesized catalysts. The surface scanning electron microscopy (Zeiss Supra Series 35VP Gemini Column of Philips XL30S model) with high resolution was used to study the surface morphology of the synthesized catalysts while the elemental composition analysis of the catalysts surfaces was conducted using an EDX detector (ZEISS supra 35 VP) attached to the SEM equipment. In order to detect the presence of surface functional species in the catalysts FTIR (Shimadzu IR prestige-21) with wave number range from 400 to 4000 cm^{-1} was used. The chemical bands between the atoms in the materials of synthesis catalysts could be evaluated by this analysis. The crystallographic structures of the synthesized catalysts were recorded by XRD using a Philips PW 1710 diffractometer, with Cu-Kα radiation ($\lambda = 1.5418$ Å) used to check the structure and unit cell of the samples. The graphite mono chromator 2θ measurement started from $2\theta = 10–90°$. High-resolution transmission electron micrographs of catalysts were obtained using a 200 kV TECNAI G 20 S-TWIN FEI field emission equipped with an EDAX system. This analysis is a microscopy technique that can show deep insights into the morphology and particle size of the solid catalysts. High resolution images with fine details can be reflected due to the high energy and small wavelength of the electron transmitted through ultra-thin specimen. The basic strengths of the materials were determined by using Hammett indicators (H_). About 25 mg of the sample was shaken with 5.0 mL of a solution of Hammett indicators diluted with methanol, and left to equilibrate for 2 h. After the equilibration, the colour on the catalyst was noted. The following Hammett indicators were used: neutral red (H_ = 6.8), bromothymol blue (H_ = 7.2), phenolphthalein (H_ = 9.3), 2, 4-dinitroaniline (H_ = 15.0), and 4-nitroaniline (H_ = 18.4).

2.4. Transesterification reaction

The transesterification of WCO with methanol was carried out in a 120 mL round-bottom flask. About 27 mL of oil with a calculated amount of methanol (with respect to the methanol-to-oil ratio) and catalysts (with respect to the weight percentage of oil) were added to the reactor. Thereafter, the flask connected to a water-cooled condenser, and the mixture was heated at 65 °C and vigorously stirred for 3 h. After the desired reaction time, the catalyst was separated from the product mixture by centrifugation. FAMEs were analysed by gas chromatography (Shimadzu 2010 Plus, Japan) equipped with a flame ionization detector (FID-2010 Plus) and capillary column (Nukol; 15 m in length, 0.53 mm in internal diameter, and 0.5 μm in film thickness). Methyl heptadecanoate was used as the internal standard. Then, 1 μL of the sample was injected, and the FAME content was calculated using the following equation [20]:

$$\text{FAME\%} = \frac{\sum A - A_{EI}}{A_{EI}} \times \frac{C_{EI} \cdot V_{EI}}{m} \times 100$$

ΣA Total peak area of the methyl ester in C_{14} to that in $C_{24:1}$;
A_{EI} Peak corresponding to methyl heptadecanoate;
C_{EI} Concentration of the methyl heptadecanoate solution (mg/mL);
V_{EI} Volume of the methyl heptadecanoate solution (mL);
M Mass of the sample (mg).

2.5. Catalyst reusability and stability

To examine catalyst reusability, the catalyst was separated from the reaction mixture (transesterification reaction of WPO under optimum conditions) by filtration, washed with methanol, and dried at 110 °C for 2 h. The catalyst was reused in the next run without further treatment. To assess catalyst stability, the optimum amount of catalyst (0.73 g) was stirred with 23 mL of methanol at 65 °C for 3 h. After catalyst recovery, methanol was mixed with 27 mL of WCO, and the reaction was carried out under the optimum conditions (65 °C for 3 h).

3. Results and discussion

3.1. Characterization of silica supported catalyst (CsM-SiO_2)

The textural properties, Brunauer–Emmett–Teller (BET) surface area, pore volume, average pore diameter and basic strength of the