



Evaluation of palm oil mill fly ash supported calcium oxide as a heterogeneous base catalyst in biodiesel synthesis from crude palm oil



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ABSTRACT

A palm oil mill fly ash supported calcium oxide (CaO) catalyst was developed to be used as a heterogeneous base catalyst in biodiesel synthesis from crude palm oil (CPO). The catalyst preparation procedure was optimised in terms of final calcination temperature and duration. The optimum catalyst preparation conditions were determined as final calcination at 850 °C for 2 h with 45 wt.% loading of calcined calcium carbonate (CaCO₃). A maximum biodiesel yield of 75.73% was achieved for this catalyst under fixed transesterification conditions. Characterisation tests showed that the catalyst had higher surface area and basic sites which favoured transesterification. The effects of catalyst loading, methanol to oil molar ratio, reaction temperature and reaction time on biodiesel yield and fatty acid methyl ester (FAME) conversion were also investigated. It was determined that transesterification conditions of 6 wt.% catalyst loading, 12:1 methanol to oil molar ratio, 45 °C reaction temperature, 3 h reaction time and 700 rpm stirring speed resulted in biodiesel yield and FAME conversion of 79.76% and 97.09%, respectively. Experimental kinetic data obtained from the heterogeneous transesterification reactions fitted the pseudo-first order kinetic model. The activation energy (E_a) of the reaction was calculated to be 42.56 kJ mol⁻¹. Key physicochemical properties of the produced biodiesel were measured and found to be within the limits set by EN 14214. The developed catalyst could feasibly be used up to three consecutive cycles after regeneration using methanol washing followed by recalcination at 850 °C for 2 h.

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1. Introduction

Heterogeneous catalysed transesterification has recently been proposed as an alternative process to homogeneous catalysed transesterification for biodiesel production. The advantages of

using heterogeneous catalysed transesterification include less wastewater generation and the ability to recycle or reuse the catalyst [1]. These advantages could potentially lead to lower production costs. Nonetheless, there are two key limitations in the use of heterogeneous catalysts. Firstly, heterogeneous catalysts have lower reaction rates as compared to homogeneous catalysts. Secondly, the catalyst surface active sites are rapidly poisoned upon exposure to ambient conditions because of chemisorption of carbon dioxide (CO₂) and water (H₂O) onto the surface sites [2]. Thus, further development of heterogeneous catalysts should focus on enhancing not only catalytic performance, but also its reusability.

Calcium oxide (CaO) has recently been reported as an active heterogeneous base transesterification catalyst due to its high basicity, low solubility and easy handling [3–6]. The use of CaO can be categorised into five main groups. The groups are neat CaO, doped CaO, mixed CaO, waste CaO and supported CaO [4]. With regard to neat CaO applications, Kouzu et al. [7] has examined the reactivity of CaO, calcium hydroxide (Ca(OH)₂) and calcium carbonate (CaCO₃) in converting soybean oil into biodiesel. Fatty acid methyl ester

Abbreviations: Al, aluminium; Al₂O₃, aluminium oxide; ASTM, American Society for Testing and Materials; BET, Brunauer–Emmett–Teller; Ca, calcium; CaCO₃, calcium carbonate; CaO, calcium oxide; Ca(OH)₂, calcium hydroxide; Ca₂SiO₄, dicalcium disilicate; CN, cetane number; CO₂, carbon dioxide; CPO, crude palm oil; DG, diglyceride; DOBI, bleachability index; E_a , activation energy; EDS, energy dispersive X-ray spectroscopy; FAME, fatty acid methyl ester; FFA, free fatty acid; FID, flame ionization detector; GC, gas chromatography; HHV, high heating value; H₂O, water; ICP-AES, inductively coupled plasma-atomic emission spectroscopy; JCO, *Jatropha curcas* oil; K, potassium; k , reaction rate constant; k_0 , pre-exponential factor; Li/CaO, lithium doped calcium oxide; MG, monoglyceride; Mg, magnesium; N₂, nitrogen; O, oxygen; P, phosphorus; R, gas constant; R², correlation coefficient; r , reaction rate; SEM, scanning electron microscopy; Si, silicon; SiO₂, silicon oxide; T, temperature; t , time; TG, triglycerides; TGA, thermogravimetric analysis; X_{ME} , conversion of methyl ester; XRD, X-ray diffraction; ZnO, zinc oxide.

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(FAME) conversions of 93%, 12% and 0% were reported for CaO, Ca(OH)₂ and CaCO₃, respectively. However, it was reported that the catalytic activity of CaCO₃ could be improved by employing thermal activation treatment such as calcination in order to remove the surface carbonates [8]. To enhance the performance of CaO, some researchers have tried doping an active ingredient onto CaO [9,10]. For instance, lithium doped CaO (Li/CaO) was examined by Alonso et al. [11] in the transesterification of sunflower oil. The authors indicated that activation of the catalyst at high temperature was essential. However, when the activation temperature exceeded 500 °C, lixiviation occurred which affected the catalytic performance. CaO has also been mixed with other oxides for transesterification. It has been reported that CaO mixed with zinc oxide (ZnO) used in the transesterification of palm kernel oil to biodiesel resulted in a high FAME conversion of 94% [12]. In another mixed CaO attempt, Zhu et al. [13] treated CaO with ammonium carbonate solution and calcined it at 900 °C to form a solid super base, which showed high catalytic activity in *Jatropha curcas* oil (JCO) transesterification. Under the optimum conditions, the conversion of JCO reached 93%. In order to develop more cost effective CaO based catalysts, waste CaO and supported CaO are preferred. Waste mud crab, cockle and chicken eggs shells were reportedly utilised as CaO based catalysts in palm olein transesterification [14–16].

Previously, CaO supported on different palm oil mill waste boiler ashes were developed and characterised by the authors for the transesterification of CPO [17]. It was found that the use of CaO supported on waste fly ash resulted in the best FAME conversion of 94.5% under fixed transesterification conditions [17]. The present study focuses on further developing and evaluating the waste fly ash supported CaO as a catalyst to convert CPO to biodiesel. Four aspects are covered in this study, all of which have not been reported in the literature before. Firstly, the wet impregnation method used in catalyst development is optimised in terms of calcination temperature and duration after metal loading. The motivation for this optimisation is to increase the catalytic performance and potentially reduce the energy consumption in catalyst preparation. Secondly, parametric transesterification experimental tests are carried out to elucidate the effects of catalyst loading, methanol to oil molar ratio, reaction time and temperature on FAME conversion and biodiesel yield. For this study, both FAME conversion and biodiesel yield are measured to evaluate the reaction process. In the majority of the reported papers on transesterification, the effectiveness of the reaction is solely judged by the FAME conversion [2,8,14,15,18–20]. Although biodiesel yield is important as an indicator of the process viability, it is seldom measured. A minority of studies have measured the biodiesel yield [13,21] or both FAME conversion and yield [22,23] in order to evaluate the transesterification reaction. The focus of the parametric tests is to determine the conditions which would result in the highest possible biodiesel yield without compromising the FAME conversion which must exceed 96.5% as specified in the European Standard EN 14214 [24]. Under optimised conditions, the key biodiesel properties are also determined. Thirdly, the transesterification kinetic using the waste fly ash supported CaO catalyst is studied in order to determine the reaction rate constant (k) and activation energy (E_a). Lastly, the reusability of this heterogeneous base catalyst is examined in light of the need for development of enhanced reusability of heterogeneous catalysts for biodiesel synthesis.

2. Materials and methods

2.1. Materials and chemicals

CPO was provided by Havys Oil Mill Sdn. Bhd., Malaysia. The accompanying sample analysis report stated that the CPO had a free fatty acid (FFA) content of 3.7%, a deterioration of bleachability

index (DOBI) value of 2.6% and a moisture content of 0.2%. Palm oil mill fly ash was collected from Seri Ulu Langat Palm Oil Mill Sdn. Bhd., Malaysia to be used as catalyst support. Methanol (>99% purity) and CaCO₃ (99.95% purity) were purchased from Merck and Sigma Aldrich, respectively. Meanwhile, an internal standard methyl heptadecanoate was purchased from Sigma Aldrich.

2.2. Catalyst synthesis

The wet impregnation method was utilised to prepare the catalyst at a fixed composition of 45 wt.% calcined CaCO₃ loaded onto palm oil mill fly ash [17]. In brief, the fly ash was first sieved and dried at 105 °C for 24 h to eradicate all moisture. Prior to use, CaCO₃ was calcined at 800 °C for 90 min to remove CO₂ and generate CaO. Subsequently, water was added to obtain the active salt precursor Ca(OH)₂. The purpose of dissolving CaO into aqueous Ca(OH)₂ was to create a suitable medium for both the CaO and fly ash to combine well during mixing. Typically, to obtain 45 wt.% calcined CaCO₃ loaded catalyst, 13.5 g of calcined CaCO₃ was added to 200 mL of pure deionised H₂O in a 3-neck flask under magnetic stirring at 700 rpm to prepare an aqueous solution of Ca(OH)₂. The solution was heated in a closed system at 70 °C to minimise water loss. 16.5 g of fly ash was then slowly added to the solution and mixed vigorously for another 4 h until a homogeneous mixture was obtained. The sample was then aged for 18 h to ensure that the Ca(OH)₂ precipitated on the fly ash carrier. The removal of adhering H₂O in the mixture was accomplished using a hot air oven at 105 °C for 24 h. A hot filtration test following the methodology given by Lempers and Sheldon [25] was carried out to confirm that the developed catalyst was heterogeneous. Briefly, the catalyst was filtered from the transesterification reaction mixture halfway through the reaction at 2 h and 80 °C (6 wt.% catalyst loading and 12:1 methanol to oil molar ratio) and the reaction was allowed to continue in the absence of the catalyst. The contribution of homogeneity was ruled out since the reaction came to a halt.

To develop a catalyst with increased catalytic activity and potentially reduce the energy consumption in catalyst preparation, the wet impregnation method used was optimised in terms of calcination temperature and duration after metal loading. The dried catalyst was calcined at temperatures of 850, 900, 950 and 1000 °C in a muffle furnace for two different durations of 2 and 5 h.

2.3. Catalyst characterisation

The basic strength of the catalysts was determined by using the following Hammett indicators: phenolphthalein ($H_- = 9.3$), 2,4-dinitroaniline ($H_- = 15$) and 4-nitroaniline ($H_- = 18.4$). Typically, 25 mg of catalyst was mixed with 1 mL of Hammett indicator diluted in 20 mL of methanol and equilibrated for 2 h. A colour change indicated that the catalyst is stronger than the indicator and vice versa [14]. The synthesised catalysts were examined by thermogravimetry analysis (TGA) using a Mettler Toledo TGA/DSC 1 system operating from ambient temperature to 900 °C at a scanning rate of 10 °C min⁻¹ under a nitrogen (N₂) flow rate of 15 mL min⁻¹. The surface morphology of the developed catalysts was analysed using scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy (EDS). The catalysts were photographed using SEM in a FEI Quanta 400F FESEM system operating at 15 kV to estimate the particle sizes and shapes. The EDS elemental composition (particularly the calcium (Ca) concentration) was semi-quantitatively expressed in terms of weight percentages using Oxford-instruments INCA 400. EDS was used due to the unavailability of more accurate quantification techniques such as inductively coupled plasma-atomic emission spectroscopy (ICP-AES). In addition, X-ray diffraction (XRD) was utilised as a quantitative determination of the CaO concentration within the catalysts

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