



# Synthesis of fatty acid methyl esters via the transesterification of waste cooking oil by methanol with a barium-modified montmorillonite K10 catalyst



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## ARTICLE INFO

### Article history:

Received 1 September 2014

Received in revised form

18 July 2015

Accepted 7 August 2015

Available online xxx

### Keywords:

Waste cooking oil

FAME

Transesterification

Montmorillonite K10

Catalyst

## ABSTRACT

The transesterification of waste cooking oil (WCO) with methanol to produce fatty acid methyl esters (FAMES) in the presence of barium-modified montmorillonite K10 (BMK10) catalyst was investigated in a batch reactor. The influence of the reaction parameters on the yield of FAME was investigated. The highest value of 83.38% was obtained with 3.5 wt% catalyst loading at 150 °C with a methanol: oil molar ratio of 12:1 during a reaction time of 5 h. BMK10 is a promising low-cost catalyst for the transesterification of WCO to produce FAME.

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## 1. Introduction

The search for renewable fuel sources to meet global energy demands has become increasingly more crucial because of the worldwide concern of global warming. The fossil fuel reserve is diminishing at an alarming rate and requires much effort to find sustainable alternative energy sources. Biodiesels have been known as one of the potential fuel substitutes derived from the relatively inexpensive renewable biological sources (vegetable oils or animal fats), which can be used extensively for powering diesel engines and utility systems [1,2]. Several advantages attributed to biodiesels include the capacity to lower greenhouse gas emissions compared with fossil fuels, biodegradation, improved lubrication, and environmentally benign nature [3].

Catalysts for transesterification can be classified into two kinds: homogeneous and heterogeneous [4]. Homogeneous catalysts have advantages over other catalysts, such as high activity, cost effectiveness, and easily attained reaction conditions [5]. However, such catalysts suffer the drawbacks of sensitivity to free fatty acids (FFAs)

and water in different oil feedstock. For example, when the FFA and water content are above 0.5% and 0.06%, respectively, the basic catalysts (KOH and NaOH) react with the FFA to produce soaps [5–7]. Therefore, oils contain high levels of FFA and water, such as waste cooking oil (WCO), which cannot be directly used to produce biodiesels by homogeneous catalysts [5]. The advantages and limitations of homogeneous and heterogeneous transesterification in oil with high FFA (mostly WCO) are discussed in detail by Ref. [8]. Therefore, it is very important to develop a heterogeneous catalyst that can process oils with high FFA and water content.

The use of heterogeneous catalysts in the transesterification and esterification of vegetable oils and FFAs with alcohols has rapidly increased. Basic or acidic catalysts are often employed for such applications. For example, a limestone-derived heterogeneous catalyst is used for the transesterification of used frying oil [9], a nanocrystalline zeolite is used as a catalyst for waste cooking palm oil [10], modified organoclay catalysts are used for the esterification of fatty acids [11], and solid base catalysts (Na<sub>2</sub>SiO<sub>3</sub>) are used to catalyze the transesterification of cottonseed oil [12]. Furthermore, the synthesis of fatty acid methyl esters (FAMES) from the transesterification of waste fruit oilseed with methanol over heterogeneous silica and a dealuminated zeolite acid-base catalyst system

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has been reported. The highest triglyceride conversion ( $\leq 96\%$ ) and biodiesel yield ( $\leq 80\%$ ) were achieved by the K-ITQ-6 catalyst (at 5 wt% loading), with an oil: methanol molar ratio of 1:20 after 24 h of the reaction at 180 °C [13]. The esterification of oleic acid over the solid acid catalyst prepared from Amazon flint kaolin was investigated. The heterogeneous acid catalysts yielded high transesterification activity (98.9%) for oleic acid at 160 °C, with an acid: methanol molar ratio of 1:60 and a reaction time of 4 h when thermally treated samples (at 850 °C and 950 °C) were activated by sulfuric acid solutions [14]. Heteropolyacid supported on acid-treated MK10 clay was employed for the esterification of levulinic acid to *n*-butyl levulinate with *n*-butanol, and 97% levulinic acid conversion was obtained [15]. The favorable clay properties, such as mechanical stability, thermal stability, high surface area, and ion exchange capacity, have attracted attention for further research [15–17]. Clay is a naturally benign substance. The use of clay as a catalyst for chemical reactions is an exciting component of green chemistry. Furthermore, clay is inexpensive, nontoxic, chemically versatile, and recyclable, as well as suitable for the industrial synthesis of naturally abundant physiologically active compounds [18–20]. The type of clay substance employed in the present study could be sourced locally. To modify commercial montmorillonite K10 (MK10) with alkaline earth metals, MK10 was utilized as a model catalyst from low-cost raw materials during FAME synthesis. Previous studies revealed that untreated montmorillonite clays have low activity and produce inactive catalysts; however, relatively mild acid-activated clays, such as commercial MK10, produce catalysts of only low activity [21,22]. Therefore, clay enhancement via modification is imperative to enrich acidic properties and circumvent the disadvantages of natural materials with respect to the relatively low activity.

The use of low-quality feedstock, such as WCO, to produce FAME will reduce the feedstock cost. Therefore, the current work focused on the synthesis of FAME by enriched MK10 with the alkaline earth metal barium as a catalyst for the transesterification of WCO with methanol because of the easy availability of both materials. The influence of the reaction parameters was investigated; these parameters included the methanol/oil molar ratio, catalyst loading, temperature, and time.

## 2. Materials and methods

### 2.1. Materials

For this study, WCO was obtained from the cafeteria of the Engineering Campus of Universiti Sains Malaysia. Methanol (HPLC-grade,  $\approx 99.9\%$ ) was used for transesterification, and *n*-hexane ( $\approx 96\%$ ) was used as a solvent for gas chromatography (GC) analysis; these reagents were purchased from Merck (Malaysia). Methyl heptadecanoate ( $\approx 99.5\%$ ) was used as an internal standard for GC and purchased from Sigma–Aldrich (Malaysia). All the reactants, MK10, barium chloride dihydrate ( $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ), and sodium bicarbonate were purchased from Sigma–Aldrich and used as received for catalyst preparation. These reagents were used for the transesterification reaction without the need for further purification, except for WCO.

### 2.2. Preparation of the BMK10 catalyst

The barium-modified MK10 (BMK10) catalyst was synthesized by a hydrolysis reaction in a metallic solution. The initial step involved the preparation of pillaring agents using 0.2 M barium nitrate solution that was partially hydrolyzed, in which 0.3 M sodium carbonate was the base to obtain the final base: metal ratio ( $\text{OH}^-/\text{M}^{n+}$ ) of 2.0 under vigorous stirring at 55 °C for 2.5 h. Stirring

was continued for an additional 6 h at room temperature. This reaction solution was aged for 24 h at room temperature. A weighed amount of MK10 (15 g) with barium in distilled water was also prepared and stored overnight. The pillaring solution after aging was treated with the clay suspension for 30 min and aged at 55 °C for 4 h. The resultant mixture was dried for 24 h and calcined at 500 °C for 5 h. Finally, the thermally treated catalyst was ground and immediately employed for the activity tests.

### 2.3. Characterization of the as-synthesized catalysts

The Brunauer–Emmett–Teller (BET) surface area measurement were carried out under  $\text{N}_2$  gas at 77 K by using Micromeritics, Model ASAP 2020, USA. Scanning electron microscopy (SEM) was performed to identify the surface morphology of the catalyst. The crystallographic structure of the catalysts were recorded by XRD using a Philips PW 1710 diffractometer. Fourier transform infrared spectrophotometry (FTIR) was used to identify the functional groups of the catalyst. An FTIR spectrophotometer (Shimadzu IRPrestige-21) was used to measure the absorption of various infrared light wavelengths emitted by the sample. Samples were ground and diluted with 0.1 wt% potassium bromide (KBr) prior to analysis.

### 2.4. Catalytic activity during transesterification of WCO by the BMK10 catalyst

The transesterification of WCO with methanol was performed in a 300 mL stainless steel batch reactor. The catalyst and the other reactants were charged into the reactor at room temperature. The content was heated to the desired temperature, as controlled by the WATLOW Series SD programmable proportional integral derivative temperature controller. Continuous mixing immediately commenced after coupling of the reactor to ensure sufficient contact between WCO, methanol, and the BMK10 catalyst. In addition, the stirrer speed was set to the maximum experimentally determined value of 700 rpm to prevent mass transfer limitations [23]. The different parameters of transesterification were evaluated in the given range for temperature (100 °C–200 °C), catalyst loading (0.5–6.5 wt%), reaction time (1–6 h), and methanol: oil molar ratio (3:1–15:1) to determine the best operating condition for the methanolysis of WCO catalyzed by BMK10. At the end of a batch reaction, the reactor contents were cooled to room temperature, and the catalyst was separated from the product mixture by centrifugation.

### 2.5. Product analysis

The centrifuged sample was analyzed by GC with a GC-2010 plus split injection unit (Shimadzu, Japan), flame ionization detector, and Nukol capillary column of 15 m  $\times$  0.53 mm  $\times$  0.50  $\mu\text{m}$ . Helium was used as the carrier gas. Each sample was analyzed by dissolving 20  $\mu\text{L}$  of FAME into 250  $\mu\text{L}$  of methyl heptadecanoate, which was used as the internal standard. Subsequently, 1  $\mu\text{L}$  of the prepared sample was withdrawn and injected into the GC apparatus from the top. The FAME content was calculated as follows:

$$\text{FAME content (\%)} = \frac{m_i A_b}{A_i m_b} \times 100 \quad (1)$$

where  $m_i$  is the mass (in mg) of methyl heptadecanoate,  $A_b$  is the total peak area from the FAME  $\text{C}_{14:0}$ – $\text{C}_{24:0}$ ,  $m_b$  is the mass of the FAME sample, and  $A_i$  is the total peak area of the internal standard.

### 2.6. Catalyst stability

The reusability of the BMK10 catalyst was tested to establish its

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