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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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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.

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_2SiO_3) 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$99.5%) was used as an internal standard for GC and purchased from Sigma–Aldrich (Malaysia). All the reactants, MK10, barium chloride dihydrate ($BaCl_2 \cdot 2H_2O$), 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 (OH^-/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 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 × 0.53 mm × 0.50 µm. Helium was used as the carrier gas. Each sample was analyzed by dissolving 20 µL of FAME into 250 µL of methyl heptadecanoate, which was used as the internal standard. Subsequently, 1 µL of the prepared sample was withdrawn and injected into the GC apparatus from the top. The FAME content was calculated as follows:

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

where m_i is the mass (in mg) of methyl heptadecanoate, A_b is the total peak area from the FAME $C_{14:0}$–$C_{24:0}$, 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 stability and capability to provide the same catalytic activity as the first run. The catalyst was collected after the transesterification reaction was completed, and the liquid mixture (methanol, methyl ester, and glycerol) was carefully decanted. The remaining solid was washed with hexane for several times to remove the adhered oil particles and then dried in an oven for 48 h at 60 °C. The catalyst was weighed and reused for a series of transesterification processes at the same operating conditions. The cycle was stopped when the yield of FAME was too low because of the decreasing amount of the recovered BMK10 catalyst after a few cycles.

3. Results and discussion

3.1. Catalyst characterization

The surface characteristics of the MK10 and BMK10 catalysts are shown in Table 1. The surface area, total pore volume, and average pore diameter decreased as barium was loaded. The diameter of the MK10 molecule was approximately 61.566 Å, which suggested the possible inclusion of the mesopores of the support. In turn, this change decreased the surface area and pore diameter. Similarly, a slight drop in the surface area was recorded during mixed oxide loading onto alumina, as reported by Amani et al. [24]. The possibility of barium multilayer formation on the support surface during metal loading could not be excluded. The partial blockage of the pores by the multilayer dispersion of metals decreased the total surface area [25,26].

The SEM micrograph of the BMK10 catalyst is shown in Fig. 1. The catalyst consisted of large and small particles, which were mainly formed by aggregated constituents that agglomerated together on the rough catalyst surface.

The interaction between barium and MK10 led to the development of a catalyst with a porous structure, which accounted for the observed high BMK10 catalytic activity of 75.95% during a short reaction time of 2 h. The elemental composition of the BMK10 catalyst was verified by energy dispersive X-ray spectroscopy (EDX) with a detector mounted on a microscope (inset in Fig. 1). The catalyst contained 55.86 wt% O, 17.51 wt% C, 10.84 wt% Ba, 9.92 wt% Si, 3.46 wt% Na, and 2.41 wt% Al. The metals silicon, aluminum, and sodium originally occurred in MK10. The higher weight percentage of barium, compared with sodium, suggested the important role of Ba as a modifier, such that the catalytic activity was improved in the transesterification reaction. The obtained FAME contents for raw clay, calcined raw clay, and the MBK10 catalyst were 6.33%, 10.12%, and 83.70%, respectively, using WCO with methanol: oil molar ratio of 9:1, catalyst loading of 3.5 wt%, and reaction time of 6 h at 150 °C.

The XRD patterns of the uncalcined and calcined BMK10 catalysts, with varied calcination temperatures from 400 °C to 700 °C are shown in Fig. 2. The XRD intensity of the prepared catalysts was changed by sintering at high temperatures when the calcination temperature was increased from 400 °C to 700 °C. Fig. 2 illustrates the characteristic peaks of SiO_2 for the catalysts. If the calcination temperature was equal to or greater than 500 °C, peaks corresponding to spinel Ca_2AlSiO_2 appeared. Therefore, the calcination temperature was fixed at 500 °C because of the intensity of the SiO_2 (20.9°, 26.68°, 39.52°, and 68.27°), Ca_2AlSiO_2 (49° and 42°), $CaSiO_2$ (33.7° and 76°) and Al_2O_3 (68° and 19°) peaks, which made the catalyst sufficiently active in the transesterification reaction (Section 3.2). In addition, the textural properties of raw clay and the prepared MBK10 catalyst with a calcination temperature of 500 °C had a high BET surface area. This result agreed with the XRD results because of catalyst activation in the transesterification reaction.

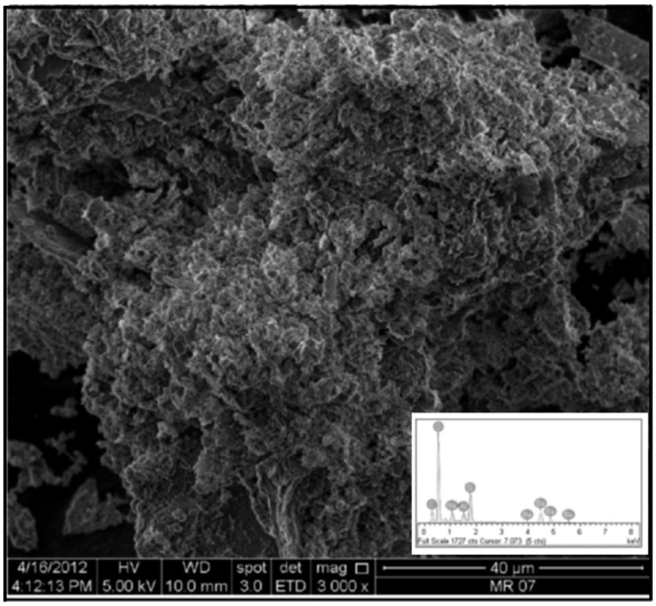

Fig. 1. Scanning electron microscopy of as-synthesized BMK10 catalyst (3000× magnification) with inset of EDX spectra.

The functional groups present on the surface of raw MK10 and BMK10 were determined by FTIR. The spectra for raw MK10 and BMK10 are shown in Fig. 3. Given the observed catalytic performance, raw MK10 and BMK10 were further characterized by FTIR analysis to obtain additional information on the catalyst surface properties. The appearance of absorption bands at the range of 3218–3854 cm^{-1} in the spectrum of raw MK10 clay showed the presence of O–H stretching and water molecules, and these bands were assigned to the stretching modes of external and internal hydroxyl groups similar to observed peaks by Zatta et al. [17]. The intensity of peaks within this range increased in the spectrum of modified clay because of the hydrolysis process during catalyst modification. The Si–O–Si stretching vibration in the spectra appeared as a strong band in the range of 1000–1100 cm^{-1} for raw MK10, and the characteristic absorption at 990 cm^{-1} was assigned to the M^+–OH band. Deformation of Si–O–M^+ and O–Si–O stretching is shown at 1630 and 1080 cm^{-1}, respectively. The observed band at 500 cm^{-1} was due to the Al–OH stretching vibration or the sulfate (SO_4) vibrational band width at 450 cm^{-1} [27]. The presence of these functional groups also contributed to high activity of the modified clay catalyst. However, both catalysts showed strong and sharp peaks in the range of 1000–1260 cm^{-1}, which represented the C–O stretching vibration. Moreover, MK10 exhibited a peak near 2320 and 800 cm^{-1}, which was assigned to the occurrence of sodium bicarbonate and silicon, respectively. Both components were present in MK10 with the chemical formula $(Na\cdot Ca)_{0.33}(Al\cdot Mg)_2(Si_4O_{10})(OH)_2\cdot nH_2O$ [28]. For the spectrum of

Table 1
Textural properties of montmorillonite K10 (MK10) and barium-modified MK10 (BMK10) catalysts.

Sample	BET surface area ($m^2\cdot g$)	Total pore volume ($cm^3\cdot g$)	Average pore diameter (Å)
MK10	126.29	0.194	61.566
BMK10	13.114	0.056	161.893

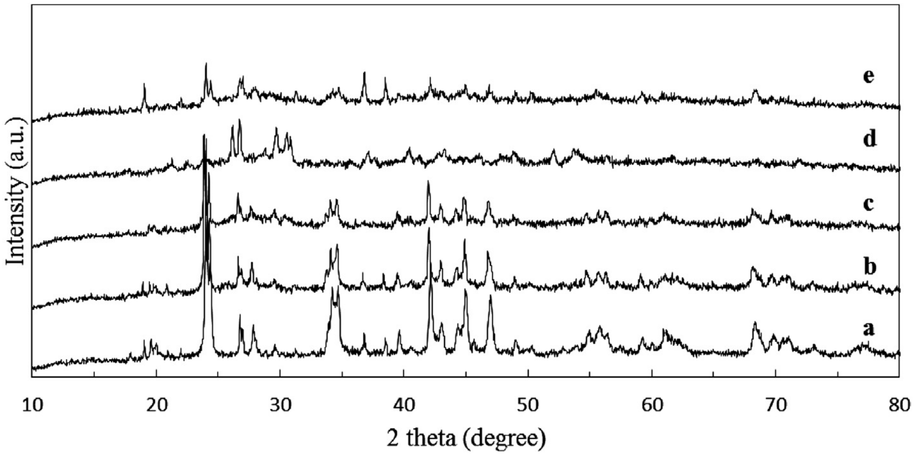

Fig. 2. XRD patterns of the uncalcined (a) and calcined (b–e) BMK10 catalysts at different calcination temperatures: (b) 400 °C, (c) 500 °C, (d) 600 °C, (e) 700 °C.

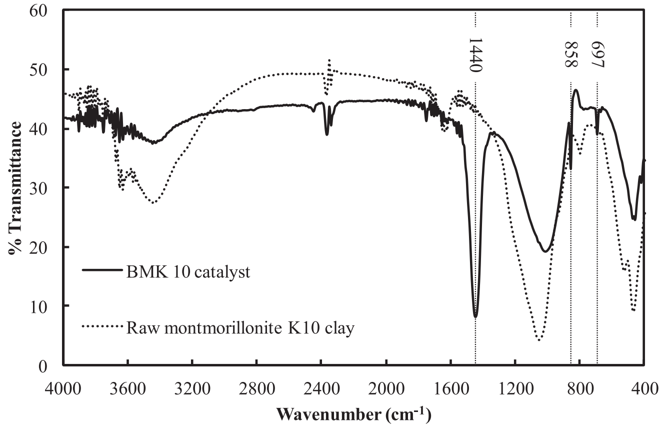

Fig. 3. FTIR spectra for montmorillonite K10 (MK10) and barium-modified MK10 catalyst.

BMK10, a weak peak near 697 cm^{-1}, a strong and sharp peak near 858 cm^{-1}, and a very strong peak near 1440 cm^{-1} indicated the presence of barium group in the modified catalyst. The appearance of a weak band at 2800 cm^{-1} and a strong peak with broad shoulder at 2400 cm^{-1} were attributed to asymmetric stretching of C–H bonds in the methyl groups and asymmetric/symmetric stretching of C–H bonds in the methylene groups, respectively.

3.2. *Effect of calcination temperature on catalyst activity*

The as-synthesized BMK10 catalyst was subjected to different calcination temperatures that varied between 400 °C and 700 °C, because calcination resulted in the formation of homogeneously dispersed mixed oxides [28] where the bonding between support and metals became stronger. The calcination temperature caused the catalyst structure to change, thereby affecting catalytic activity and FAME content. The effect of the calcination temperature on catalytic activity was investigated in the transesterification of WCO at 150 °C, methanol: oil molar ratio of 9:1, stirring speed of 700 rpm, and 3.5 wt% catalyst loading based on a certain amount of oil for 6 h. Fig. 4 shows the effect of different calcination temperatures on the FAME content. The FAME content peaked at 78.61% when the calcination temperature increased to 500 °C, and the content decreased (12.59%) with further increase in temperature (700 °C). As the calcination temperature increased, the molecules that covered the surfaces of clay support were successively desorbed based on the strength of interaction with active sites; the interaction between support and barium metal was established [29]. The observed high activity could be attributed to the well-dispersed barium metal in the clay matrix. Thus, we inferred that the reduction in activity for catalyst calcined at higher temperature (>500 °C) was due to the collapse of BMK10 structures, which led to undesirable surface changes. The collapsed structures left the inert mixture incapable in catalyzing the transesterification reaction. The decrease in activity was previously reported [30], in which the basic strength and activity of the LiOH-intercalated montmorillonite catalyst decreased when calcined above 450 °C. Significant losses of porosity and basicity were attributed to excessive loss of hydrated water. Thus, the calcination temperature of 500 °C was selected for further investigations in the current research.

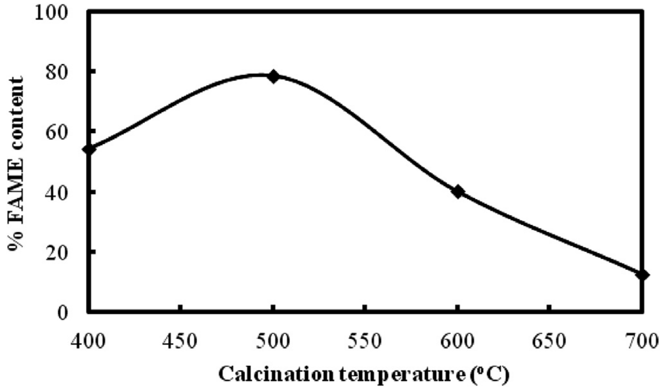

Fig. 4. Effect of calcination temperature for BMK10 catalyst on the transesterification of WCO at the following reaction conditions: temperature = 150 °C; methanol: WCO molar ratio = 9:1; catalyst loading = 3.5 wt%, and reaction time = 6 h.

3.3. *Effects of various parameters on the reaction*

3.3.1. *Influence of the reaction temperature on FAME content*

The influence of the reaction temperature on FAME content during the transesterification of WCO with methanol was investigated at different temperatures ranging from 100 °C to 200 °C using BMK10 as catalyst for 6 h with 3.5 wt% catalyst loading and methanol:oil molar ratio of 9:1. The reaction temperature was found to influence the FAME content, as shown in Fig. 5. The FAME content (82.05%) increased with the reaction temperature up to

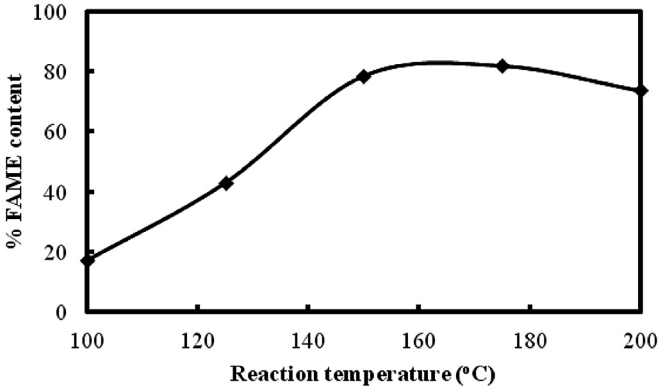

Fig. 5. Effect of reaction temperature for BMK10 clay catalyst on the transesterification of WCO at a methanol: WCO molar ratio of 9:1 and catalyst loading of 3.5 wt%.

175 °C and then decreased when the temperature increased further. This finding proved that the FAME content was dependent on the reaction temperature. High temperatures facilitated the mass transfer of reactor contents and dispersion of the catalyst particles. High temperatures also increased interactions between the catalyst with protons generated from alcohol solvent and mixed oxide catalyst with the alkyl group of triglycerides and fatty acid-forming nucleophile, followed by rearrangement and proton transfer, resulting in high conversion to products [31]. The decrease in the FAME content at temperatures exceeding 175 °C might be due to the gasification of methanol at high temperature, which reduced the amount of FAME in liquid form or reactants. Although 175 °C resulted in a maximum FAME content, the reaction temperature of 150 °C was chosen for further investigations because only a marginal increase in the FAME content (3.44%) was obtained with a large difference in temperature (25 °C). Low reaction temperatures are believed to be more economically favorable considering the less energy input required.

3.3.2. *Effect of reaction time on FAME content*

The transesterification reaction of WCO was performed at different durations ranging from 1 h to 6 h to study the effect of the reaction time on the FAME content. The other reaction parameters with BMK10 catalyst remained constant as follows: methanol: oil molar ratio of 12:1, 3.5 wt% catalyst loading, and 150 °C. Fig. 6 shows the effect of the reaction time. A sufficient reaction time was crucial to obtain a high FAME content in transesterification, because a rapid increase in FAME content was only observed after a certain time period required for the formation of a sufficient amount of these triglyceride derivatives. Therefore, the FAME content increased with time until a point where the changes in the FAME content were no longer significant. In the study of Karabas [32] on acorn kernel oil methyl ester, they confirmed that the reaction time has the strongest influence on production. Thus, an increase in the FAME content was observed from 1 h to 5 h, and the FAME content was unchanged after a reaction time of 5 h. A difference of only 0.52% in the FAME content was observed between the reaction times of 5 and 6 h. The FAME content was only 54.16% when the reaction time was only 1 h, and it was considered quite low compared with the FAME content obtained from a longer reaction time. The transesterification reaction did not reach equilibrium within such a short time period. Mixing and dispersion between reactants might not be sufficient to produce a high FAME content. As the reaction time increased, more contact time between reactants and catalyst became available, which led to more frequent collision. The formation of FAME during the transesterification reaction was more favorable at such operating conditions. A slight decrease in the FAME content at 6 h might be due to reverse transesterification, in which FAME formation was no longer favorable. The increase in FAME yield with time was proven by Ngamcharussrivichai et al. [33], who reported a FAME yield of 27.2% at a reaction time of 2 h, and the highest yield of FAME (99.9%) from palm kernel oil using Ca(NO$_3$)$_2$-modified dolomite catalyst was 3 h at 10 wt% catalyst loading and methanol: oil molar ratio of 15:1.

3.3.3. *Effect of methanol:WCO molar ratio*

The effect of the WCO:methanol molar ratio was studied through transesterification using BMK10 as a catalyst for 6 h at 150 °C with 3.5 wt% catalyst loading, 700 rpm stirring speed, and different WCO:methanol ratios ranging from 1:3 to 1:15. Transesterification to convert WCO and methanol into glycerol and biodiesel had a stoichiometric ratio of 1:3 (WCO:methanol). Given that the reaction was reversible, excess amounts of methanol shifted the equilibrium of the reaction to produce more FAME and increase oil conversion. Fig. 7 shows the effect of different WCO: methanol molar ratios. The FAME content peaked at 83.26% with oil: methanol molar ratio of 1:12 because of the pushing effect of excess methanol on the reaction balance, which suggested that the molecules of WCO had more interactions with large amounts of methanol. A decrease in oil conversion was observed after the ratio of 1:12 was obtained, because large amounts of methanol will dilute oil and reduce the reaction rate. A decrease in oil conversion also led to depreciation in FAME quality and allowed the reaction to

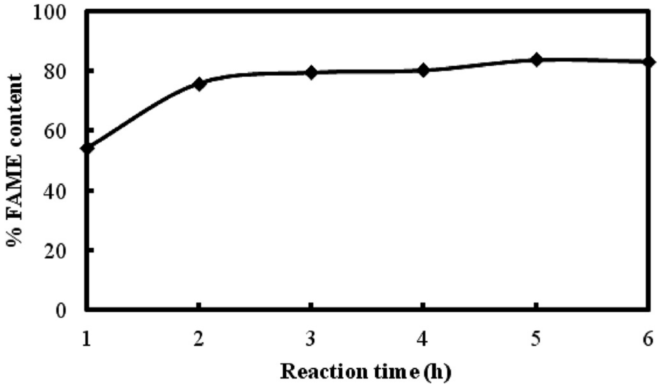

Fig. 6. Effect of reaction time on the transesterification of WCO at the following reaction conditions: temperature = 150 °C; methanol: WCO molar ratio = 12:1, and catalyst loading = 3.5 wt%.

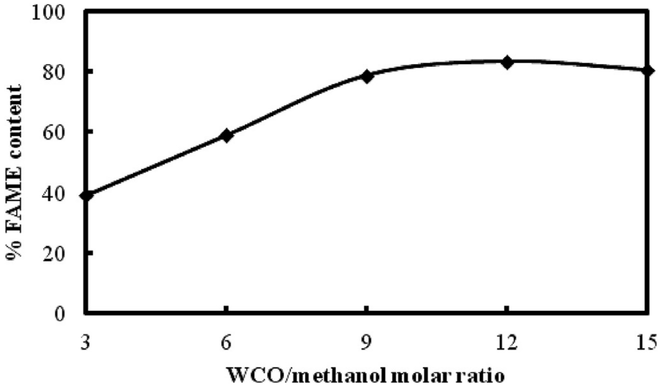

Fig. 7. Effect of the methanol: WCO molar ratio on the transesterification of WCO at the following reaction conditions: temperature = 150 °C; reaction time = 6 h, and catalyst loading = 3.5 wt%.

occur at low temperature. Thus, excess methanol was effective to a certain extent only in increasing oil conversion. The optimum amount of methanol required should be obtained as large amounts of methanol need additional separation and might be hazardous to the environment [28].

3.3.4. *Effect of catalyst loading*

To study the effect of catalyst loading on the FAME content, the transesterification reaction of WCO was carried out with different catalyst loading ranging from 0.5 wt% to 6.5 wt% of oil using BMK10 catalyst for 5 h at 150 °C with a methanol: WCO molar ratio of 12:1. Fig. 8 shows the effect of catalyst loading on the FAME content. An increase in FAME content was observed from 0.5 wt% to 3.5 wt% of oil with maximum FAME content of 83.78%. This result was due to the increase in amount of available catalytic active sites as the amount of catalyst increased. Oil conversion at the catalyst loading of 0.5 wt% was very low (25.04%) because the insufficient amount of catalysts resulted in incomplete conversion of the triglycerides into fatty acid esters [34]. However, the FAME content decreased when catalyst loading was increased to more than 3.5 wt%. Only a certain amount of catalyst was sufficient to react with a particular amount of methanol and WCO. Low concentration of catalyst loading was only favorable with low methanol: oil molar ratio for high FAME yield. When the amount of catalyst was in excess, mass transfer between catalyst and reactants decreased, thereby reducing the interactions between them and simultaneously reducing the amount of FAME. This finding might be due to the undesired reaction between triglycerides and the alkali catalyst to form more soap. Catalyst loading of 3.5 wt% showed the highest FAME content, so it was selected as the optimum catalyst loading and used for further investigation in the present research.

3.4. *Catalyst stability*

For the three successive reactions carried out at 150 °C, 12:1 methanol: oil molar ratio, and 3.5 wt% catalyst loading for 5 h, the FAME contents were 83.78%, 78.30%, and 21.50%, respectively. The observed decline might be due to the blockage of catalyst active sites by high-molecular-weight triglycerides. Moreover, catalyst losses occurred during the recovery process, causing a reduction in the catalyst actives sites. This factor was one of several that caused a decrease in the FAME content. Leaching test for the catalyst was carried out by contacting the catalyst with methanol at 150 °C for 6 h. The FAME content of 13.01% was obtained when the used methanol reacted with WCO, which indicated that leaching of the catalyst was present but of considerably low value. This factor led to the reduction in the FAME content for several runs during the transesterification reactions. The observed trend was corroborated by the work of Chin et al. [35].

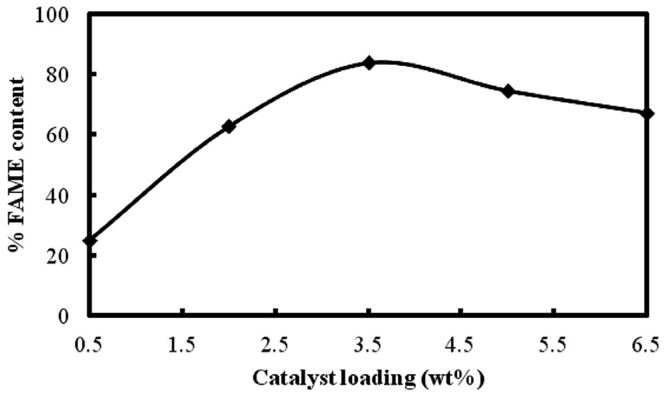

Fig. 8. Effect of catalyst loading on the transesterification of WCO at the following reaction conditions: temperature = 150 °C; reaction time = 5 h, and methanol: WCO molar ratio = 12:1.

4. Conclusions

The transesterification of WCO using BMK10 as catalyst was investigated. Results showed that the use of modified natural inorganic materials as catalysts was found to be highly active toward transesterification and able to obtain 83.38% of FAME at 3.5 wt % catalyst loading, temperature of 150 °C, methanol: oil molar ratio of 12:1, and reaction time of 5 h. The effects of various parameters on the reaction were discussed. The decrease in catalytic activity after two reaction cycles was observed, suggesting that organic residues were not completely removed from the catalyst during washing. Moreover, losses that occurred during the recovery process resulted in the reduction of catalyst active sites.

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