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Transesterification of moringa oleifera oil to biodiesel over potassium flouride loaded on eggshell catalyst

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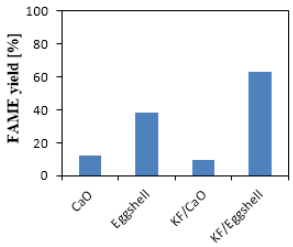
GRAPHICAL ABSTRACT



ABSTRACT

In recent years, biodiesel has received great attention in the production of engine fuel. Biodiesel can be produced by esterification reaction, transesterification reaction or both esterification and transesterification reactions of non-edible oil. However, high production cost of biodiesel is a remaining problem. Therefore, a low-cost and reliable feedstocks for biodiesel production such as moringa oleifera as non-edible plant oils could be a potential of alternative fuel. In addition, waste eggshell can be a good candidate as a low-cost catalyst for the reaction. In this study, potassium fluoride (KF) loaded on calcium oxide (CaO) and eggshell were prepared. The catalysts were characterized by X-ray Powder Diffraction (XRD), Fourier Transform Infrared (FTIR) spectroscopy, Field Emission Scanning Electron Microscope (FESEM) and nitrogen adsorption-desorption analysis. The biodiesel productions (fatty acid methyl esters, FAME) were carried out in a batch reactor with different parameters such as temperature (50°C- 60°C), molar ratio of methanol to oil (4-6), reaction time (1-3 hours) and KF loading (1wt%- 25wt%) on eggshell. Maximum FAME yield of 94.2% is observed on KF/eggshell with 5% of catalyst amount, 6:1 molar ratio of methanol to oil, 50°C reaction temperature, 1 hour reaction time and 1% of KF loading is observed to be optimum for better conversions. Therefore, the KF/eggshell catalyst has been proven to be a promising catalyst for biodiesel production which is simple, economical and efficient.

Keywords: Moringa oleifera oil, biodiesel, transesterification, eggshell, potassium fluoride

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1. INTRODUCTION

Biodiesel is biodegradable, renewable, non-toxic, possesses inherent lubricity, relatively high flash point, and reduces most regulated exhaust emissions compared to petrodiesel [1]. In order to decide which type of reaction suitable to produce biodiesel, the free fatty acid value of the feedstock oil must be considered [2]. Rather than using the non-edible oil as a solution to reduce the cost [3], low-cost catalyst such as eggshell can be used to make the biodiesel production more economical and sustainable [4, 5].

Many researchers have been employed solid basic catalysts for transesterification reaction owing to its eco-friendly and efficient for biodiesel production. Highly biodiesel production can be obtained under mild conditions and it is generally takes shorter time for completion [6]. A few researchers have tried to load an active ingredient such as lithium, sodium and potassium onto CaO [4]. For instance, Watkins et al. [7] prepared a series of lithium-impregnated calcium oxide catalysts and studied the transesterification of glyceryl-tributyrate to methyl butyrate and glycerol. CaO exhibited poor catalytic activity in transesterification, with 2.5% conversion, whereas 1.23% Li loading on CaO enhanced the catalytic activity to 100% conversion in 20 min. Thus, a heterogeneous catalyst of alkali-doped metal oxide has appeared to be a promising candidate to replace conventional homogeneous catalysts for biodiesel production.

In the present work, KF loaded on eggshell and CaO were synthesized by impregnation method. The structure and properties of the catalysts were characterized by XRD, FTIR, BET surface area analyzer and FESEM studies. The catalytic activity was evaluated through the transesterification of moringa oleifera oil. The influence of various factors on the biodiesel yield such as such as methanol to oil molar ratio, reaction temperature and reaction time were also investigated.

2. EXPERIMENTAL

2.1 Catalyst preparation and characterization

The waste eggshells were washed by deionized water to remove dust and impurities. The sample was then soaked in the hot water for 2 hours in order to remove the white membrane in the eggshell. Then, the sample was dried and grinded into powder form. The sample was then dried at 110 °C for 2 hours followed by calcination at 820 °C for 4 hours in air. This sample is denoted as eggshell. The KF loaded on eggshell and CaO catalysts were prepared by impregnation

of eggshell and commercial CaO powder with potassium fluoride aqueous solution. The resulting slurry were heated slowly at 80 °C under continuous stirring and maintained at that temperature until nearly all the water being evaporated. The solid residue was dried in at 110 °C overnight followed by calcination at 873 K for 3 h in air. The KF/eggshell was also prepared with various KF loading (1, 5, 10, 15 and 25 wt%).

The crystalline structure of the catalyst was determined with X-ray diffraction (XRD) recorded on a powder diffractometer (Bruker Advance D8, 40 kV, 40 mA) using a Cu Ka radiation source in the range of 2h = 1.5–90. Field Emission Scanning Electron Microscope (FESEM) was used to obtain information about the morphology of the samples. The morphology study of the catalysts was carried out using a JEOL scanning electron microscope model JSM-6701F. The FTIR spectra were recorded in KBr (0.3% w/w) disks in the wavelength region of 4000–400 cm^{-1} with an Agilent Cary 640 FTIR spectrometer. The BET surface area analyses of the catalysts were determined by N_2 adsorption–desorption isotherms using a Quantachrome Autosorb-1 instrument.

2.2. Transesterification of moringa oleifera oil

Transesterification of moringa oleifera oil with methanol were carried out in a transesterification reactor with three-neck round bottom flask fitted with an overhead stirrer and water-cooled reflux condenser. The reactor was also equipped with an oil bath with digital temperature controller for heating purpose. Then, 1.5 g of catalyst was suspended in a required volume of methanol and heated until a desired temperature of reaction was achieved. The reaction mixture was stirred for required time duration. Upon completion of the reaction, the solution was then transferred into a separating funnel. The solution was left to settle to separate into two layers. Next, the clear part in the separating funnel was injected three times to three different vials. The sample was centrifuge at 2500 rotation per minute for 15 minutes. The samples for further analysis were prepared from the upper part of the clear biodiesel phase. The transesterification of moringa oleifera oil was carried out under different reaction conditions in order to optimize the reaction, such as KF loading from 1 to 25 wt%, reaction time from 1 to 3 h, reaction temperature from 50 °C to 60 °C and methanol to oil ratio from 4:1 to 6:1.

A gas chromatography, GC (Agilent 6890) fitted with split inlet and flame ionization detector (FID) and DB-WAX (30 m × 0.15 mm) capillary column was used for quantitative analysis of the product obtained. Methylheptadecanoate was used as internal standard. The temperature of GC oven was programmed as initial temperature of 120 °C for 0.5 minutes and increases at heating rate of 15 °C/min up to 220 °C for 1 minute. The temperature was increases again at heating rate of 30 °C/min up to 250 °C for 5 minutes and then cooled down to 50°C for 0.5 minutes.

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of eggshell, CaO and KF/eggshell and KF/CaO. Both eggshell and CaO showed identical patterns with the diffraction peak at 32.23°, 37.4° and 53.86°. According to previous studies [8], these main three peak were respected to Miller index of (111), (200) and (220), respectively. However, the crystallinity of both bare eggshell and CaO catalysts were disturbed markedly by the introduction of KF due to the compression of support (eggshell and CaO catalysts) structure by KF incorporation. On the other hand, it is suggesting that the supports could not retain their structure after KF introduction resulting in the formation of KF containing phase [9]. New peak at 35.17° and 45.94° were also observed indicating the presence of $Ca(OH)_2$ which might be due to the incomplete formation of $Ca(OH)_2$ from CaO.

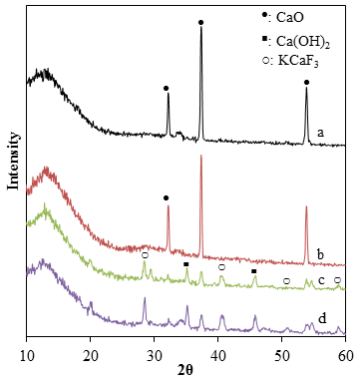

Fig. 1 XRD patterns of (a) eggshell, (b) commercial CaO, (c) KF/eggshell and (d) KF/CaO.

As shown in Figure 2, different KF loading on eggshell catalysts were characterized by XRD. Based on result, as the percentage of KF loadings increased from 1 to 5 wt.%, the intensity of (200) peaks of CaO were increased and later decreased as KF loading increased to 25 wt.%. The introduction of KF on eggshell was lead to the formation of new crystal structure of $KCaF_3$ which located at 28.74, 41.22, 51.26 and 59.52°. The intensity of the peak was clearly intensified as KF loading was increased to 25 wt%. The $KCaF_3$ was formed during the impregnation stage [10] probably following the equation as:

$$CaO + 3KF \leftrightarrow KCaF_3 + K_2O \quad (1)$$

The formed K_2O was not stable and reacted with water in the impregnating solution following the equation as:

$$K_2O + H_2O \leftrightarrow 2KOH \quad (2)$$

The formed KOH was crystallized on the surface of the catalyst and decomposed at high temperature under the catalysis of eggshell. The equation is:

$$2KOH \xrightarrow{\text{eggshell} + \Delta} K_2O + H_2O \quad (3)$$

However, there was no obvious X-ray diffraction peak of K_2O in Figure 2 at 2θ =31° [11]. The same situation also occurred in the X-ray diffraction patterns of the nanocatalysts made from CaO and KF [10]. It might be because most K_2O was dispersed in the catalyst due to the interaction between CaO (in the eggshell) and KF, and only a very limited excessive amount of K_2O was crystallized on the external surface.

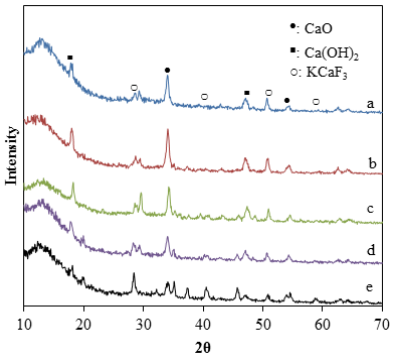

Fig. 2 XRD patterns of different percentage KF loadings on eggshell. (a) 1 wt.% KF, (b) 5 wt.% KF, (c) 10 wt.% KF, (d) 15 wt.% KF, and (e) 25 wt.% KF.

The BET surface area and total pore volume of all catalysts are summarized in Table 1. KF/CaO has the highest surface area followed by CaO, eggshell and KF/eggshell. The discrepancy in surface area of KF/eggshell and KF/CaO may be due to pore blockage in eggshell by KF. Similar result was reported about the decrease of surface area of fresh KOH/Al_2O_3 and KOH/NaY catalysts with the increase of KOH loading amount [12]. It is reasonable that the BET surface area decreased after introduction of KF into eggshell catalyst. However, our result showed that the BET surface area and total pore volume of the KF/CaO catalyst were higher than that of the CaO catalyst. This might be due to the chemical reaction between KF and CaO in the formation of new crystal $KCaF_3$. As depicted in Fig. 1d, the intensity of the $KCaF_3$ is higher in KF/CaO than in KF/eggshell. Therefore, high amount of $KCaF_3$ in KF/CaO might lead to the generation of pores on the surface of CaO.

Table 1 BET surface area and total pore volume for all catalysts.

Catalyst	BET Surface Area (m^2/g)	Total Pore Volume (cm^3/g)
CaO	12	0.0729
Eggshell	8	0.0350
KF/CaO	19	0.0779
KF/eggshell	6	0.0556

The textural images of eggshell, KF/eggshell and KF/CaO catalysts were depicted in Figure 3. All catalysts showed agglomeration of particles CaO and eggshell. Based on the observation, the size of the eggshell particle was greater than CaO which is more than 1 µm. This may lead to the lower surface area of eggshell compared to CaO as in agreement to the BET surface area of the catalysts. While, small particles distributed on eggshell and CaO were attributed to the active $KCaF_3$ crystals. These active $KCaF_3$ crystals were shown to be well distributed on the surface of eggshell compared to the CaO which showed the agglomeration of active $KCaF_3$ crystals.

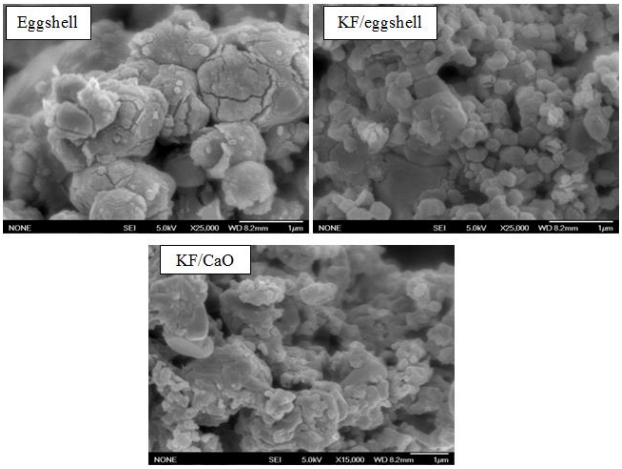

Fig. 3 FESEM images of eggshell, KF/eggshell and KF/CaO catalysts.

The catalysts were analysed using FTIR in single crystal potassium bromide mode in order to determine the functional group that present on the catalyst. Based on Figure 4, the strong band at 3645 cm^{-1} indicates the O–H bonds from the remaining hydroxide or maybe from water molecules on the external surface of the samples during handling the sample to record the spectra [13]. The broad band around 1430 cm^{-1} and a weak band at 870 cm^{-1} are corresponding to the C–O bond related to carbonate species [14]. Boro et al. [9] had also observed the similar band ranges for calcium carbonate present in their study for CaO catalyst. New band was also observed at 717 cm^{-1} which is attributed to the presence of KF on CaO and eggshell.

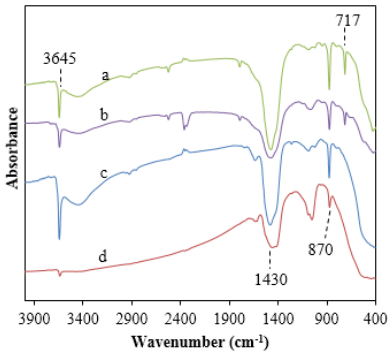

Fig. 4 FTIR spectra of (a) KF/CaO, (b) KF/Eggshell, (c) CaO, and (d) eggshell catalysts

Figure 5 shows the effect of reaction temperature on the FAME yield. The results indicated that raising reaction temperature had negative effect on the reaction. The most

suitable temperature for transesterification reaction was at 50 °C which showed about 30% yield of FAME. This result is an accord to the previous study done by Kafuku et. al. [15] which stated the suitable temperature of transesterification of moringa oleifera oil is 50 °C. This temperature is below the boiling point of methanol and thus the methanol can reacts completely with the oil. Meanwhile, 10% and 20% yield of FAME were produced and at 55 °C and 60 °C, respectively. Low FAME yield at these reaction temperatures were might be due to the loss of some methanol at temperature close to the methanol boiling point.

The effect of molar ratio of methanol to oil on biodiesel yield was examined under 5% w/w catalyst of oil at 50 °C. Figure 6 showed the relationship between the molar ratio of methanol to oil and biodiesel yield over 25 wt% KF/eggshell. The result showed inconsistency of molar ratio of methanol to oil with biodiesel yield. Highest FAME yield was obtained at 6:1 methanol to oil molar ratio followed by 4:1 and 5:1. This result is in agreement with previous study done by Rashid et. al. [1] and da Silva et. al. [16]. At low methanol to oil molar ratio, the reaction may not completed as poor separation of methanol and oil was observed in the separating funnel. This experiment demonstrates that the suitable molar ratio between methanol and oil is 6:1.

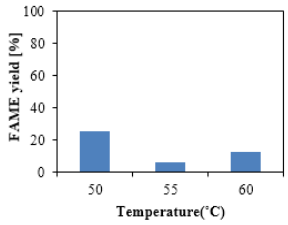

Fig. 5 Effect of reaction temperature on biodiesel yield over 25 wt% KF/eggshell. Reaction conditions: molar ratio of methanol to oil 4:1, catalyst amount 5 wt.% and reaction time 1 h

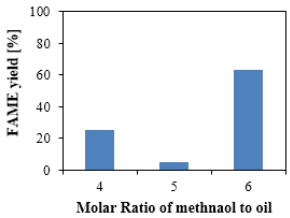

Fig. 6 Effect of molar ratio of methanol to oil on biodiesel yield over 25 wt% KF/eggshell. Reaction conditions: reaction temperature 50°C, catalyst amount 5 wt.% and reaction time 1 h.

Figure 7 shows the yield of FAME at different reaction times from 1 to 3 hours in reaction temperature of 50 °C, catalyst amount of 5 wt% and molar ratio methanol to oil of 6:1. It was observed that increasing the reaction time from 1 to 3 hours lead to the decreasing of FAME yield. The reaction time of 1 hour makes the highest yield of FAME. Kafuku et. al [15] has also agreed that the optimal transesterification reaction time is 1 hour. Based on observation, longer reaction time will lead to soap formation because of hydrolysis of esters which tends to cause more fatty acids to form soap. This indicates that 1 hour was the best reaction time for FAME production using *Moringa Oleifera* oil.

From the result above, the optimized condition of transesterification reaction was at 50°C, molar ratio methanol to oil 6:1 and 1 hour of reaction time. Under these conditions, transesterification reaction of moringa oleifera oil was studied using different type of catalysts as shown in Figure 8. For bare catalysts, eggshell catalyst produces higher FAME yield (40%) than commercial CaO catalyst (13%). The introduction of KF on CaO gave a negative effect on the reaction which reduced the FAME yield to 10% which may be due to the agglomeration of $KCaF_3$ crystals on CaO as depicted on FESEM image in Figure 3.

While, for KF/eggshell, the result gave better yield which gave 63% of FAME yield. The addition of KF to eggshell improves the catalytic ability and improves saponification resistance. On the other hand, the addition of KF has led to the formation of $KCaF_3$ active crystal, which is more efficient. Since fluorine has greater electronegativity than oxygen, the Ca^{2+} in $KCaF_3$ is a stronger Lewis acid that has stronger attraction for CH_3O. Simultaneously, F is a stronger Lewis base with stronger attraction to H^+. So, $KCaF_3$ converts CH_3OH to CH_3O more easily than does CaO. The surface of the catalyst KF/eggshell gathers more CH_3O, which makes it easier to attack carbonyl carbon and leads further to increase of rate and efficiency of transesterification [10]. High FAME yield of KF/eggshell may be due to the well distribution of active $KCaF_3$ crystal as depicted in FESEM image in Figure 3. Therefore, the KF/eggshell with well distributed active $KCaF_3$ has higher catalytic activity than KF/CaO.

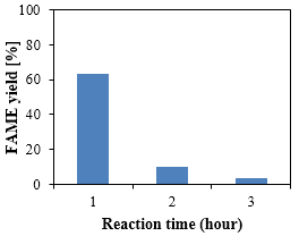

Fig. 7 Effect of reaction times on biodiesel yield over 25 wt% KF/eggshell. Reaction conditions: reaction temperature 50°C, catalyst amount 5 wt% and molar ratio of methanol to oil 6:1.

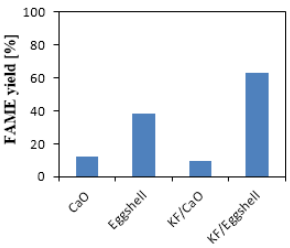

Fig. 8 Effect of catalysts types on biodiesel yield over 25 wt% KF/eggshell. Reaction conditions: reaction temperature 50°C, catalyst amount 5 wt%, molar ratio of methanol to oil 6:1 and 1 hour of reaction time.

In order to improve the FAME yield, different loading of KF on eggshell was also examined. As shown in Figure 9, highest FAME yield was observed on 1wt% of KF on eggshell resulted about 90% of FAME yield. However, the introduction of 5 wt% KF on eggshell gave tremendous reduction to only 2% of FAME yield. The FAME yield was observed to increase slowly when the loading was increased to 10% KF and 15% KF which gave 6% and 7% of FAME yield, respectively. For 25% KF loading, sudden increase of FAME yield was observed which gave 64% of FAME yield. The decrease percentage of FAME yield in KF loading higher than 1wt% might be due to excessive KF loading covers on active sites of catalyst surface, resulting in the decrease of catalytic activity [17]. Thus, 1wt% of KF loading provide the best KF loading on eggshell for FAME production.

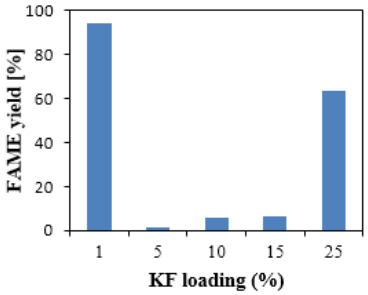

Figure 9 Effect of different KF loading on eggshell on biodiesel yield. Reaction conditions: reaction temperature 50°C, catalyst amount 5 wt%, molar ratio of methanol to oil 6:1 and 1 hour of reaction time.

4. CONCLUSION

KF loaded with eggshell, which was prepared by simple impregnation method followed by calcination at a high temperature in air, showed high catalytic activities for the transesterification reaction. This approach was successfully used in an attempt to increase the catalytic activity of commercial CaO via green CaO utilized by eggshell waste as catalyst support for the transesterification reaction. The catalyst with 1 wt% KF loading on eggshell was found to be the optimum catalyst, which gave the best catalytic activity. Under the optimal conditions of transesterification reaction over 1wt%KF/eggshell, i.e., a 6:1 molar ratio of methanol to oil, a catalyst amount of 5 wt% and 50°C, the FAME yield reached 90% after 1 h of reaction. The preparation of KF/eggshell catalyst is simple, economical and efficient, and this catalyst seems to be a promising catalyst for biodiesel production.

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