JOURNAL OF OLEO SCIENCE

# Hydrogel-Templated Solid Base Catalysts for Transesterification of Soybean Oil

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**Abstract: A new method for utilization of hydrogel is proposed here for the preparation of solid base catalysts for the transesterification of vegetable oil. When a solution of KF is mixed with a solution of $Ca(NO_3)_2$, $CaF_2$ is obtained and inactive as a catalyst in the transesterification of vegetable oils. The catalysts were synthesized by the sequential incorporation of KF and/or $Ca(NO_3)_2$ solutions into the hydrogel upon microwave irradiation and then the as-obtained hydrogel was calcined at 800℃ for 5 hours to eliminate the template and yield catalysts for the biodiesel productions. The prepared catalysts obtained by the different ways in the incorporation of ions into the hydrogel showed different physical properties and catalytic activities in the transesterification of soybean oil. All catalysts, except the low concentration of $Ca(NO_3)_2$, exhibiting the high activity yielding more than 90% FAME after 1 hour at 65℃, using oil to methanol molar ratio of 1:15 and 10 wt% of catalyst amounts.**

**Key words:** biodiesel, solid base catalyst, hydrogel, transesterification

## 1 INTRODUCTION

Renewable energy or green energy sources can be converted directly into liquid fuels - biofuels for transportation needs (cars, trains, trucks, and buses). Biodiesel is a common renewable fuel produced from waste vegetable oils and animal fats for use in diesel engine[1, 2]. In addition, biodiesel, an alternative fuel that is green to environment because of its biodegradability, biorenewable nature, very low sulfur content, low volatility, and balancing carbon dioxide in atmosphere[3]. The production of biodiesel is widely proceeded through transesterification reaction catalyzed by homogeneous catalysts or heterogeneous catalysts. The most notable homogeneous catalyst used in the transesterification reaction is alkaline catalysts such as KOH, NaOH, $CH_3ONa$ and $CH_3OK$. In contrast to homogeneous catalysts, heterogeneous catalysts[4] are easily removed from the reaction mixture leading the facile purification step and the quality of biodiesel. As a result, the development of heterogeneous catalysts for the production of biodiesel is of great importance. Metal oxide support or natural solid waste such as eggshells, bone, and manure are used as catalysts for the production of biodiesel. The limitations of these catalysts are sensitive to water and also quite expensive. Therefore, the adaptation of heterogeneous catalysts should be more efficient and cheap for bio-diesel productions.

In this research, the synthesized solid base catalyst was obtained from the utilization of hydrogel as a template. Metal oxides, especially alkali earth oxides have been studied extensively because of their suitable basic strength. Heterogeneous catalysts are generally impregnated with KF or $K^+$ ion to increase the catalytic performance. These catalysts are the highly active for the transesterification reaction in production of biodiesel. KF-doped solid oxides; for example, $KF/ZnO$[5], $KF/Al_2O_3$[6], $KF/Eu_2O_3$[7], KF/hydrotalcite[8], $KF/CaO$[9, 10], $KF/Zn(Al)O$[11], $KF/CaO-MgO$[12], $KF/Ca$-Al hydrotalcite[13], $KF/Ca_xAl_2O_{(x+3)}$[14], KF/Mg–Fe bi-metal oxides[15], $KF/Mg$-La[16], $KF/Si$-MCM-41[17], $KF/CaO–Fe_3O_4$[18], $KF/clam shells$[19], $KF/CaO$ (lime mud)[20], and KF/clay[21] have been reported to be efficient heterogeneous catalysts for transesterification of vegetable oils. Moreover, synthesized catalysts of KF with $Ca^{2+}$ could form new $KCaF_3$ phase that was probably the active specie for the enhancement of catalytic activity[9, 10, 13, 22]. Niju *et al.* found that KF on CaO leads to the formation of $KCaF_3$, which enhanced catalytic activity[19]. Other solid supports have been developed from waste biodegradable products by utilizing imperfectly carbonized natural products; for instance, eggshell[23–30], biont shell[31], cockle shell[32], crab shell[33], fish scale[34], shrimp shell[35], snail shell[36], scallop shell[37], chicken manure[38],

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seashell[39], and cellulose[40]. Here, a hydrogel was used as a model template for a new synthesis of solid base catalyst due to its facile incorporation of ions into the structures of hydrogel (the left-handed helical structure)[41] upon microwave irradiation and the hydrogel can be removed by calcination to new phase and morphology of heterogeneous catalysts. Recently, hydrogel was used as a template to produce gold, silver nanoparticles[42], and iron oxide nanoclusters[43] with microwave irradiation in which the mung bean starch noodle or mung bean vermicelli was used as hydrogel[44, 45]. In this study, heterogeneous catalysts were prepared by the incorporation of KF and $Ca(NO_3)_2$ into the hydrogel and the prepared catalysts were tested for the transesterification reaction of soybean oil.

## 2 EXPERIMENTAL PROCEDURES

### 2.1 Chemicals and Materials

Potassium fluoride (KF), calcium nitrate ($Ca(NO_3)_2$, and methanol were purchased from Sigma Aldrich. Hydrogel (mungbean vermicelli) and soybean oil were purchased a local market in Thailand.

### 2.2 Catalyst Preparation

In general, three steps were used for the incorporation of KF and/or $Ca(NO_3)_2$ into hydrogel for catalysts preparation; $(i)$ 50 cm³ of 2.5 mol/dm³ KF solution was added into 20 g of hydrogel then heated the mixture in microwave oven at 100 W for 3 minutes, $(ii)$ adding 50 cm³ of $Ca(NO_2)_3$ into the mixture and heat it in a microwave oven for 3 minutes, $(iii)$ KF solution was added to the mixture before it was heated in a microwave oven for 3 minutes. The final step, the mixture of each step (or method) washed with water and calcined at 800℃ for 5 hours. Thus, the catalysts consist of three types that are one-step (only KF with hydrogel), two-step (KF and then $Ca(NO_3)_2$ with hydrogel), and three-step catalysts (KF (1st-time), $Ca(NO_3)_2$, KF (2nd-time)) with hydrogel) and all step were calcined at 800℃ for 5 hours. The experiments of each step were shown in Scheme 1.

### 2.3 Catalyst Characterization

The basic strength of the solid bases ($H\_$) was determined by using Hammett indicator. The following Hammett indicators were used: bromthymol blue ($H\_ = 7.2$), phenolphthalein ($H\_ = 9.8$), 2,4-dinitroaniline ($H\_ = 15.0$), and 4-nitroaniline ($H\_ = 18.4$). X-ray diffraction was carried out on D8 Advance Bruker analytical system operating at the Cu $K_{\alpha1}$ ($\lambda = 1.5406$ Å) at 40 mA and 40 kV. The Data were collected over a $2\theta$ range of 20-85°. Scanning Electron Microscopy (SEM) was obtained on a JEOL JSM-6301F microscope. Fourier Transform Infrared (FTIR) spectra of the samples were recorded on a Perkin Elmer spectrometer in the range of 400 to 4000 cm$^{-1}$. A standard KBr technique was used for the sample preparation. Brunauer-Emmett-Teller (BET) surface area was measured with $N_2$ as adsorbate at 77.4 K by Quantachrome Autosorb-1. The chemical composition of sample surface was investigated by X-ray photoelectron spectrometer (XPS; AXIS ULTRA$^{DLD}$, Kratos analytical, Manchester UK.). The base pressure in the XPS analysis chamber was about $5 \times 10^{-9}$ torr. The samples were excited with X-ray hybrid mode $700 \times 300$ μm spot area with a monochromatic Al $K_{\alpha1,2}$ radiation at 1.4 keV.
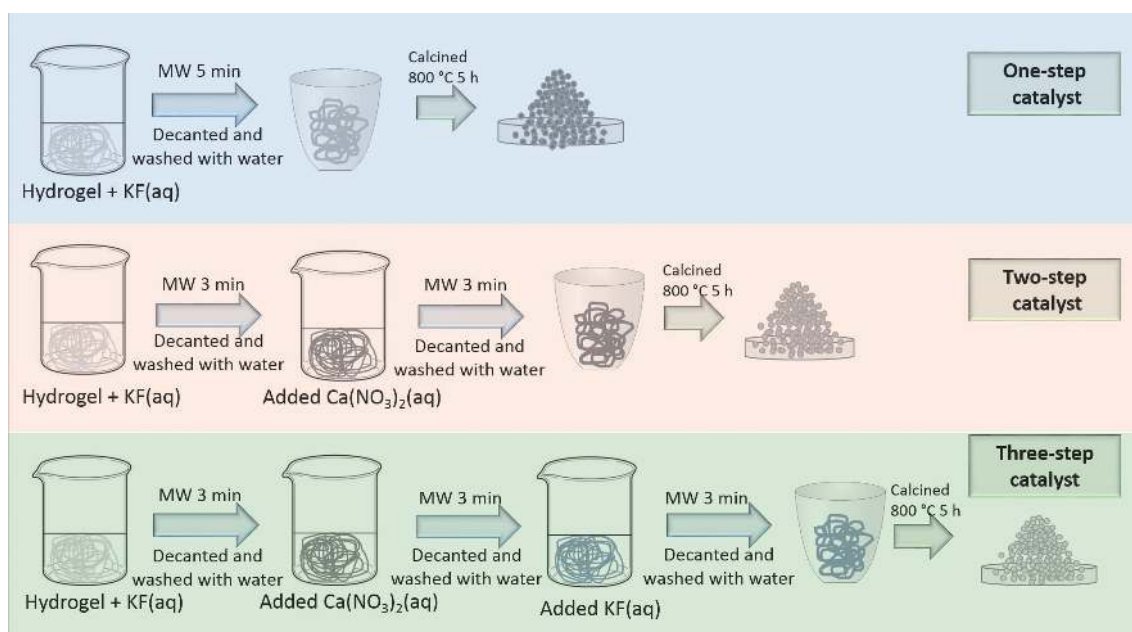


Scheme 1　The incorporation of KF and $Ca(NO_3)_2$ into the hydrogel upon microwave irradiation.

X-ray anode was run at 15 kV 10 mA 150 W.

## 2.4 Transesterification Reaction

The experiments were performed in a 100-cm$^3$ two-necked round-bottom flask equipped with a water-cooled condenser, thermometer, and mechanical stirrer. Firstly 10 g of soybean oil was warmed at 65℃ for 10 minutes and then a mixture of methanol and catalyst was added to the reaction. A reaction condition was as follows: 1:15 molar ratio of oil to methanol, 1 g of the catalyst amount, 65℃ of the reaction temperature, and 1 hour of the transesterification time. After the reaction, the catalyst was separated from the product mixture by filtration. The product of transesterification reaction was separated into two phases; top layer is the biodiesel phase of methyl esters and upper layer is glycerol. The biodiesel was washed by gently mixing warm distilled water in separatory funnel. This process was repeated until the water separated out quickly and then removing water with sodium sulfate $(Na_2SO_4)$. The biodiesel was transferred to a beaker and gently heated until it dried. The methyl ester was analyzed by $^1$H Nuclear Magnetic Resonance spectroscopy $(^1$H NMR$)$[46, 47] and Gas Chromatography $(GC)$ with HP-Innowax and FID detector[48, 49]. After each cycle of reaction, the catalyst was separated and washed several times with methanol and *n*-heptane. The resultant dried solid was calcined at 800℃ for 5 h and reused in a new batch transesterification process.

# 3 Results and discussion

## 3.1 Catalyst preparation and characterization

The catalyst preparation for incorporation of KF and $Ca(NO_3)_2$ into the hydrogel and the prepared catalysts were tested for the transesterification reaction of soybean oil as shown in **Scheme 2**. When a solution of KF is mixed with a solution of $Ca(NO_3)_2$, $CaF_2$ is obtained as solid precipitate which is not active in the transesterification of vegetable oils as shown in **Table 1**. A hydrogel was chosen a good template for the absorption of ions and the incorporation of ions into its structure was carried out by microwave irradiation[42, 43]. The incorporation of KF and $Ca(NO_3)_2$ into the hydrogel upon microwave irradiation was carried out and then the hydrogel with absorbed ions was calcined at 800℃ under air atmosphere. As shown in **Scheme 1** and **Table 1**, the first type of catalyst, a one-step catalyst, was prepared by the incorporation of 2.5 mol/dm$^3$ KF into the hydrogel $(entry 3)$. The second type of catalyst was two-step catalysts prepared by the incorporation of 2.5 mol/dm$^3$
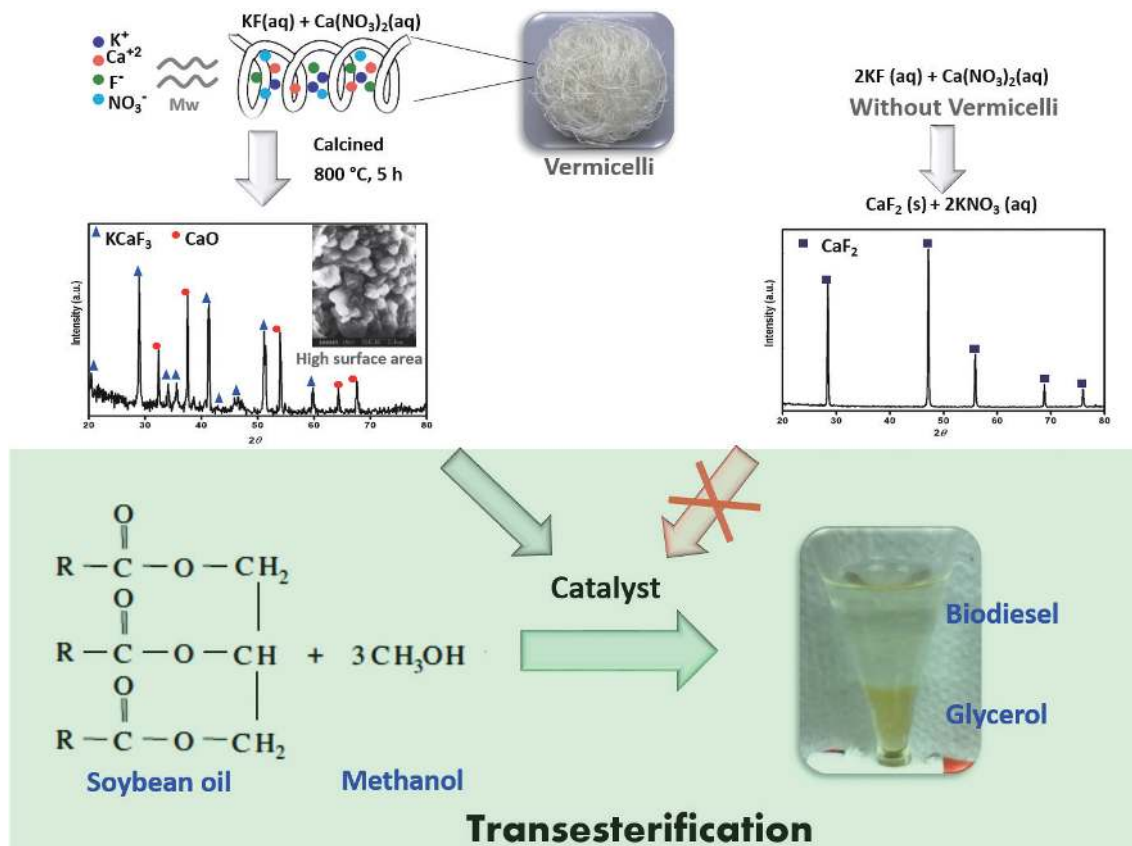


Scheme 2   The preparation of catalysts and $CaF_2$ for testing the biodiesel productions.

Table 1  Basic strength of prepared catalysts and their biodiesel yields.

| Entry | Catalyst | No. of Steps of Added Salts | Concentration of Incorporated Salts (mol/dm³) *in order* | | | Support or Template | Basic Strength (H_) | FAME Yield[a] (%) |
|---|---|---|---|---|---|---|---|---|
| | | | KF | Ca(NO₃)₂ | KF | | | |
| 1 | **A** | 0 | – | – | – | CaF₂ | 7.2 – 9.8 | 0 |
| 2 | **B** | 1 | 2.5 | – | – | CaF₂ | < 7.2 | 0 |
| 3 | **C** | 1 | 2.5 | – | – | Hydrogel | 7.2 -15.0 | 96 |
| 4 | **D** | 2 | 2.5 | 3 | – | Hydrogel | 7.2 -15.0 | 99 |
| 5 | **E** | 2 | 2.5 | 2.5 | – | Hydrogel | 7.2 -15.0 | 97 |
| 6 | **F** | 2 | 2.5 | 1.25 | – | Hydrogel | 7.2 -15.0 | 97 |
| 7 | **G** | 3 | 2.5 | 2.5 | 2.5 | Hydrogel | 7.2 -15.0 | 96 |
| 8 | **H** | 3 | 2.5 | 1.25 | 2.5 | Hydrogel | 7.2 -15.0 | 95 |
| 9 | **I** | 3 | 2.5 | 0.625 | 2.5 | Hydrogel | 7.2 -15.0 | 96 |
| 10 | **J** | 3 | 2.5 | 0.3 | 2.5 | Hydrogel | 7.2 – 9.8 | 94 |
| 11 | **K** | 3 | 2.5 | 0.1 | 2.5 | Hydrogel | 7.2 – 9.8 | 90 |
| 12 | **L** | 3 | 2.5 | 0.01 | 2.5 | Hydrogel | 7.2 – 9.8 | 75 |

[a] Determined by $^1$H NMR

All catalysts were prepared by incorporation of salts and calcination at 800℃ under atmosphere for 5 hours. Transesterification condition: oil/methanol molar ratio, 1:15; catalyst amount, 10 wt.%; reaction time, 1 hour; reaction temperature, 65℃.

KF and then Ca(NO₃)₂ at different concentrations (entries 4-6). The last type of catalyst was three-step catalysts prepared by the incorporation of 2.5 mol/dm³ KF, then Ca(NO₃)₂ at different concentrations, and reincorporation of 2.5 mol/dm³ KF before the calcination at 800℃ under air atmosphere (entries 7-12). Even though the one-step catalyst showed a good performance on the catalytic activity with 96% FAME yield, this catalyst was moisture-sensitive and soluble in water. Therefore, the second addition of Ca(NO₃)₂ was expected to stabilize the catalysts. The reaction of KF and Ca(NO₃)₂ usually yields insoluble CaF₂ as a product which is inactive for biodiesel productions. Therefore, the sequential incorporation of KF and/or Ca(NO₃)₂ into the hydrogel was expected to yield other species which were different from the direct mixing. In our study, CaF₂ was chosen as a reference support for biodiesel productions (entries 1 and 2). The hydrogel template was removed by calcination to yield active species for biodiesel productions. The hydrogel was expected to block the formation of CaF₂ after incorporation of two solutions. The reincorporation of KF solution was carried out in order to interact with free Ca²⁺ which was left in the hydrogel structure.

The basic strengths of catalysts were measured by Hammett method. Catalysts **A** and **B** (entries 1 and 2) showed the lowest basic strength at the range of 7.2 – 9.8 range and less than 7.2, respectively and they were inactive for transesterification of soybean oil. One-step and two-step catalysts showed more strongly basic sites or the basic strength at a wider range of 7.2-15.0 (entries 3-6). Three-step catalysts at higher incorporated concentrations of Ca(NO₃)₂ (entries 7-9) showed the higher basic strength than ones at lower concentration of incorporated Ca(NO₃)₂ (entries 10-12).

Some prepared catalysts were selected for the further studies. Two-step and three-step catalysts showed different compositions of potassium (K) and calcium (Ca) based on XRF measurements as shown in **Table 2**. At the same concentration of added Ca(NO₃)₂ (entries 5 and 7, **Table 1**), the two-step catalyst (Catalyst **E**) had higher Ca amount than the three-step catalyst (Catalyst **G**). The two-step catalyst especially catalyst **E** showed unexpectedly the highest surface area among other prepared catalysts (**Table 2**). Both two-step and three-step catalysts showed the pore size in the range of mesoporous types (2 nm < d < 50 nm). The one-step catalyst (Catalyst **C**) showed the XRD patterns as the phase of KF (2θ = 29.3, 33.8, 48.5, 58.1, 60.4, 70.9, 80.7) as shown in **Fig. 1a**. In addition, the phases of KCaF₃ and CaO were observed for the two-step catalysts as shown in **Figs. 1b** and **c** while decreased Ca(NO₃)₂ concentration, only the phase of KCaF₃ was observed for the three-step catalysts as shown in **Figs. 1e** and **f**. The active species of two-step catalysts was KCaF₃ because the phase of CaO was disappeared for the catalyst **H** but the high conversion was still obtained. Kaur and Ali studied KF impregnated CaO/NiO catalyst for transesterification that 5% KF in CaO/NiO found the CaF₂ and KCaF₃ phases. The higher 10% KF concentration obtained the only KCaF₃ phase and concluded the higher activity of 20% KF/CaO/NiO catalyst due to the KCaF₃ formation[50]. Thus, the for-

Table 2 Surface area and pore size of two-step and three-step catalysts.

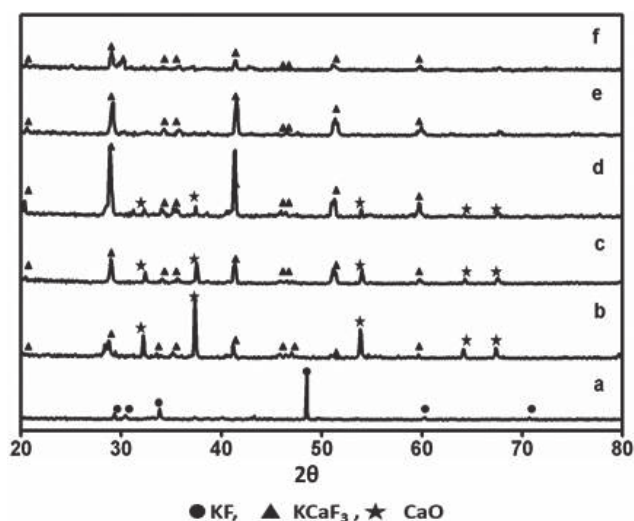| Catalyst | Composition (%) | Surface area ($m^2/g$) | Pore volume ($cm^3/g$) | Pore size (nm) | Fresh (%) | Reuse (%) |
|---|---|---|---|---|---|---|
| Two-step catalyst E | K = 14, Ca = 73 | 867.5 | 0.14990 | 31.4 | 97 | 87 |
| Two-step catalyst D | K = 11, Ca = 78 | 218.2 | 0.01696 | 24.6 | N.A. | N.A. |
| Three-step catalyst G | K = 36, Ca = 39 | 68.98 | 0.00599 | 23.4 | 100 | 18 |

N.A. = Not Available



Fig. 1 XRD patterns of (a) one-step catalyst **C**; (b) two-step catalyst **E**; (c) two-step catalyst **F**; (d) three-step catalyst **G**; (e) three-step catalyst **H**; and (f) three-step catalyst **I**.
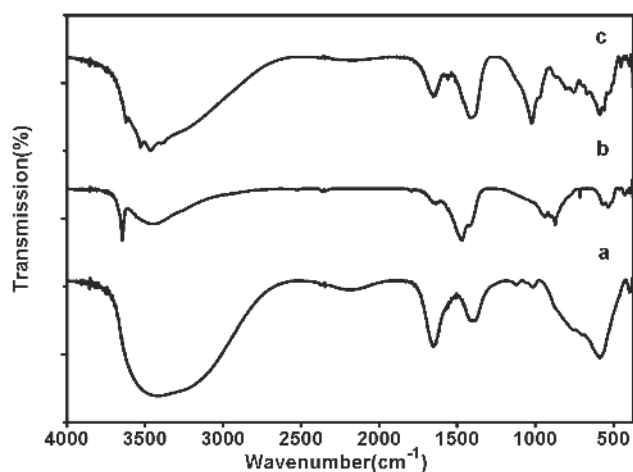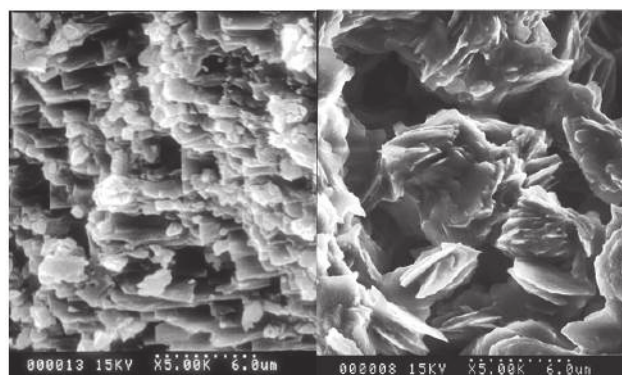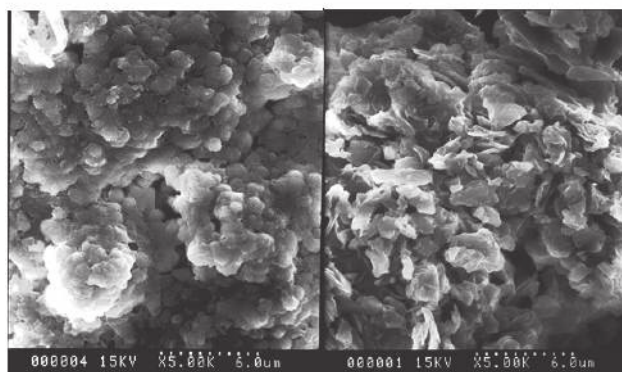


Fig. 2 FTIR spectra of catalysts; (a), catalyst **C**, (b), catalyst **D**, and (c), catalyst **F**.



(a)      (b)



(c)      (d)

Fig. 3 SEM images of (a) two-step catalyst **E**, (b) three-step catalyst **H**, (c) three-step catalyst **J**, (d) three-step catalyst **K**.

mation of new $KCaF_3$ phase might be the main reason for the enhancement of catalytic activity[9, 10, 14, 22]. The phase of CaO in three-step catalysts was disappeared as decreasing the concentration of $Ca(NO_3)_2$.

FTIR spectra of catalysts were shown in **Fig. 2**. The one-step catalyst showed FTIR bands at 1500 $cm^{-1}$, 1670 $cm^{-1}$ and a broad band at 3300 $cm^{-1}$. The broad band here indicated strong moisture adsorption on the surface of catalysts. The two-step catalyst **D** showed that the band of O-H stretching vibration was much sharper than the two-step catalyst **F**. The morphologies of catalysts were characterized by SEM as shown in **Fig. 3** that clinging sheets and small particles were observed for each catalyst. **Table 2**
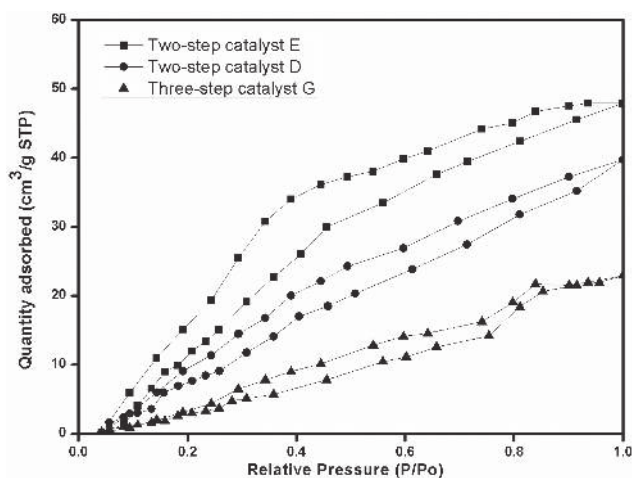
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Fig. 4 Nitrogen adsorption - desorption isotherms of two-step catalyst **E**, two-step catalyst **D** and three-step catalyst **G**.



Fig. 5 TGA of the mung bean starch with and without incorporation of KF and/or $Ca(NO_3)_2$.

shows the surface area of two-step (218.2 and 867.5 $m^2/g$) and three-step catalysts (68.98 $m^2/g$). The surface area of the commercial CaO was 3 $m^2/g$. Niju *et al.* obtained the surface area of 7.98 $m^2/g$ for KF/CaO catalyst[19]. Kaur and Ali obtained the surface area of 2.6 $m^2/g$ for 5% KF impregnated CaO/NiO catalyst. They concluded that the increase in the surface area could be due to the appearance of defects in calcium oxide structure upon impregnating potassium fluoride[50]. In this work, it was clear that the observed morphology was resulted from the removal of the hydrogel during the calcination resulting to the pronounced high surface area especially catalyst **E** at 867.5 $m^2/g$. **Figure 4** shows the $N_2$ adsorption–desorption isotherms of two-step catalyst **E**, **D**, and three-step catalyst **G**, and it exhibits a typical IUPAC type IV pattern with the presence of a hysteresis loop. These results suggest that are characterised by mesoporous structures[51]. TGA curves of the mung bean starch with and without incorporation of KF and/or $Ca(NO_3)_2$ into the hydrogel are shown in **Fig. 5**. The initial decomposition temperatures of hydrogel and KF and/or $Ca(NO_3)_2$ with the hydrogel occurred at 189 and 200°C that exhibited the release of the physically absorbed water. The second as a major weight loss in the range of 300–700°C was the decomposition of starch. The mung bean starch was decomposed completely with no carbon residue at 800°C, which is similar to other previous reports[52].

XPS spectra of the C 1s, O 1s, F 1s, K 2p, and Ca 2p for catalyst **E** (two-step) and catalyst **G** (three-step) are shown in **Fig. 6**. The binding energy of C 1s at 285 eV was assigned to C-C[53] that was found as the major component of C 1s in catalyst **E** and **G**. Interestingly, catalyst **E** showed the higher C-C component than catalyst **G**. The peaks of Ca 2p for catalyst **E** and catalyst **G** were found at 346.8 eV and 347.0 eV, respectively, corresponding to the binding
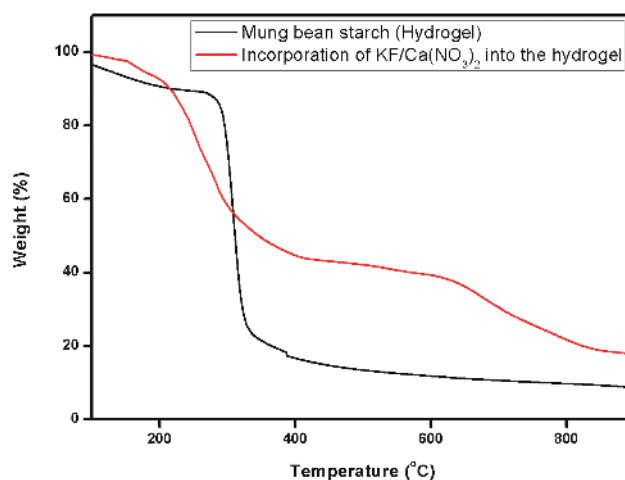
energies reported for CaO in the range 346.3-347.5 eV[54]. In addition, the peaks of O 1s at 530 eV were also found for both catalyst **E** (530.7 eV) and catalyst **G** (530.9 eV) assigned as the binding energy of O of CaO. The F 1s spectrum of catalyst **E** showed two peaks at 683.0 eV and 683.9 eV while one of catalyst G showed only one peak at 683.8 eV corresponding to the $K^+$ and $F^-$ interaction. The binding energy of fluoride of $CaF_2$ usually shows at 684.4 eV[55]. The F 1s spectrum at 683 eV was assigned as the binding energy of fluoride of $KCaF_3$. The K $2p_{3/2}$ spectra of both catalyst **E** and **G** showed two peaks indicating the presence of free $K^+$ (294.5-295.1 eV) and unfree $K^+$ (295.5-296.0 eV) where catalyst **G** had the higher amount of free $K^+$.

## 3.2 Transesterification of soybean oil

Even though catalyst **C** showed a high conversion of the transesterification at 96% yield of FAME, this catalyst showed a strong adsorption of moisture from the atmosphere as confirmed by FTIR (**Fig. 2a**) and a good dissolution in methanol. Therefore, the one-step catalyst may not be used as a heterogeneous catalyst for biodiesel productions. The incorporation of $Ca(NO_3)_2$ into the hydrogel at the second step resulting to the formation of active species and less moisture-sensitive than the one-step catalyst for biodiesel productions. Both two-step and three-step methods showed the high conversions of the transesterification. These catalysts exhibited the basic strength ($H\_$) at wider range of 7.2-15.0 which indicated the present of active species to more than one species (CaO and $KCaF_3$). Furthermore, at the same concentration of KF, as decreasing the concentration of $Ca(NO_3)_2$, the conversion of these catalysts started to abate to 75% at 0.01 $mol/dm^3$ of $Ca(NO_3)_2$ which this basic strength range ($H\_$) was 7.2-9.8. The basic strength value of catalyst influenced to the conversion of the transesterification reaction which high basic
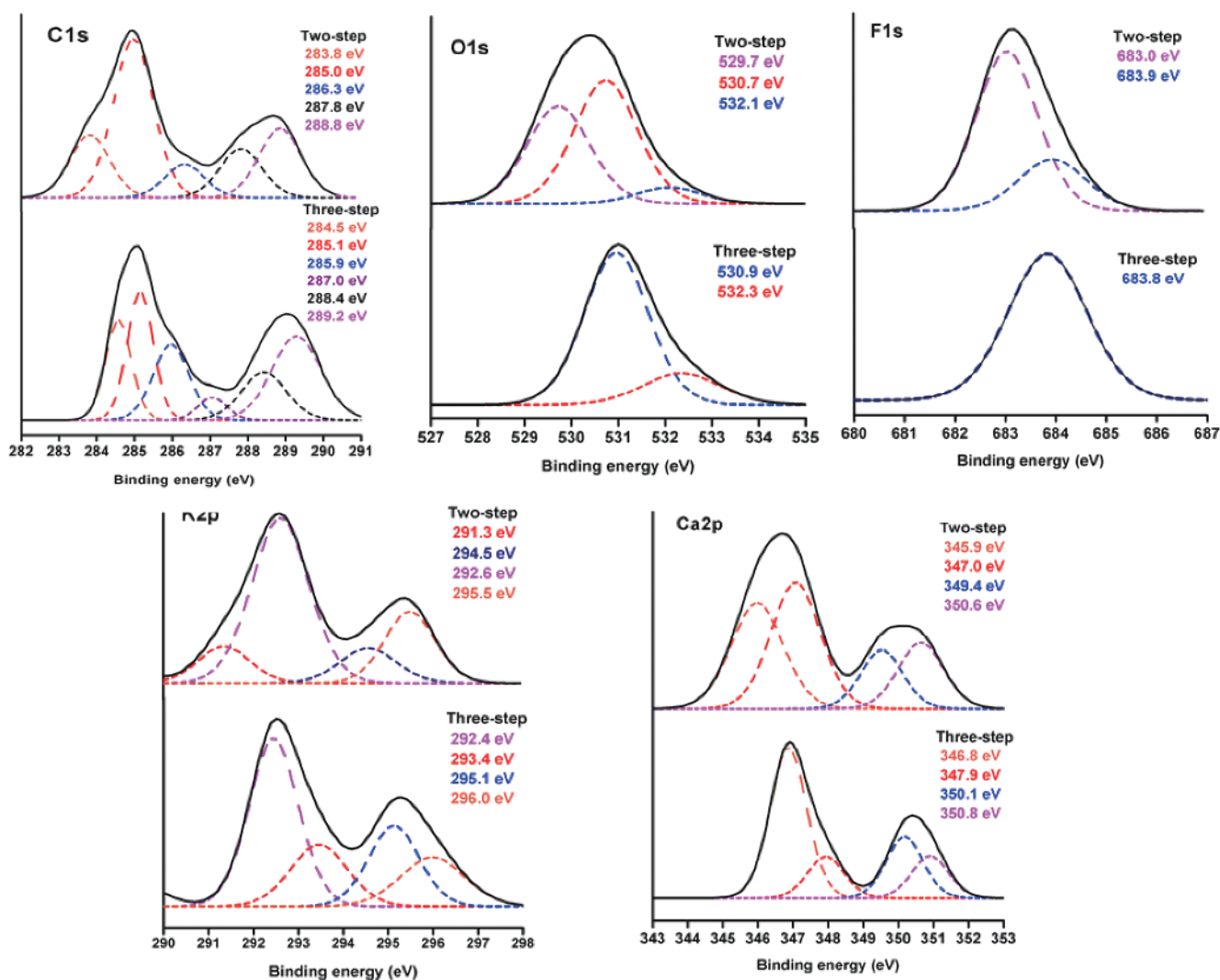
**Fig. 6** XPS spectra of the C 1s, O 1s, F 1s, K 2p, and Ca 2p for two-step catalyst **E** and three-step catalyst **G**.

strength value increased the catalytic activity as well[17, 56, 57]. The lower basic strength of the catalyst **B** without the assistant of the hydrogel ($H\_< 7.2$) showed no conversion of the transesterification reaction of vegetable oil. On the other hand, catalyst **C** with the assistant of the hydrogel showed the higher conversion of the transesterification.

The performance of catalysts was evaluated by leaching experiments by stirring catalysts in methanol for a period of time[58]. Then undissolved and dissolved parts were separated for the transesterification tests. The first part was the undissolved catalyst while the other part was the leached active species in methanol or homogeneous part. Both parts were used to test whether they were active catalysts for biodiesel productions. If the leached active species were highly dissolved in methanol, the heterogeneous catalyst would reduce the activity of the catalyst. The leaching experiments of the two-step and three-step catalysts are shown in Table 3. The leaching of both two-

step and three-step catalysts was detected as the dissolution part in methanol showed the catalytic activity for the transesterification. The three-step catalyst showed relatively much more dissolution of active catalysts in methanol than the two-step catalysts. This is consistent with the higher percentage of free $K^+$ for catalyst **G** as shown by XPS data. Thus, the two-step catalysts showed higher stability compared to the three-step catalyst.

The influence of catalyst amount in transesterification reaction is shown in Table 4. As increasing the catalyst amount of both two-step and three-step catalysts, the conversions of transesterification vegetable oils were increased but the two-step catalyst **E** showed the higher conversion than the three-step catalyst **G**. As shown in Fig. 7, the influence of reaction time was also investigated; the conversion of the two-step catalyst **E** was higher than the one of three-step catalyst **G** (58% and 35% at 2.5 minutes, respectively). In addition, the two-step catalyst **E** was very

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Table 3   Leaching of two-step and three-step catalysts.

| Catalyst | Conversion[a] (%) | |
|---|---|---|
| | Undissolved catalyst (solid phase) | Dissolution in methanol (liquid phase) |
| Two-step catalyst E | 84.24 | 57.83 |
| Two-step catalyst D | 50.27 | 5.12 |
| Three-step catalyst G | 78.64 | 94.57 |

[a] Determined by ^{1}H NMR

Table 4   Conversion of two-step catalyst E and three-step catalyst G at each catalyst amount.

| Catalyst amount (wt%) | Conversion[a] (%) | |
|---|---|---|
| | Two-step catalyst E | Three-step catalyst G |
| 2.5 | 63 | 21 |
| 5 | 87 | 37 |
| 10 | 97 | 97 |

[a] Determined by ^{1}H NMR
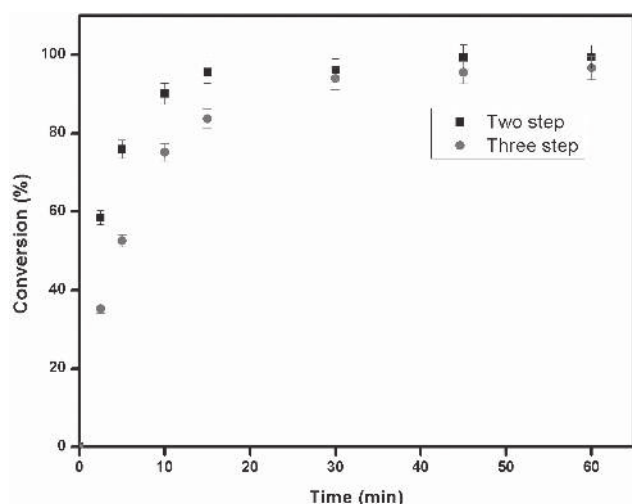


Fig. 7   Two-step catalyst G and three-step catalyst G, influence of reaction time on conversion.  Reaction condition: catalyst amount 10%, methanol/oil molar ratio 15:1.

active with the conversion of 96% for 15 minutes. Thus, the two-step catalyst was more appropriate to be utilized as a heterogeneous catalyst as confirmed from the leaching, reuse and the study on the catalyst amount. The reaction rate will be determined by the basic strength and the number of accessible active sites on the surface. As shown in Table 5, the larger surface area provides much more accessible active sites of $KF/Ca(NO_3)_2$ hydrogel enhanced the reaction rate and explained the stronger catalytic activity than that of other catalysts[59−62]. Recyclability study of two-step catalyst E on the biodiesel production is illustrated in Fig. 8. One can see that the reduction of the FAME

conversion in each cycle could be explained by the deactivation of active sites due to their poisoning by some molecules present in the reaction mixture such as ion-exchange between alkali cations with protons and natural adsorption of reactants and products in the system. It indicated a significant reduction of the number of active sites on the catalyst[63, 64].
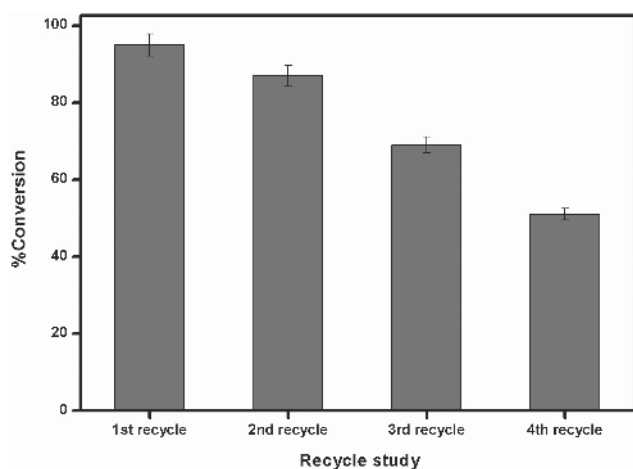
### 3.3  Kinetic of the transesterification reaction

Kinetic studies of transesterification of soybean oil in the presence of two-step catalyst, E were investigated by GC chromatography as shown in Fig. 9. The effects of temperature and time were investigated to determine the reaction kinetics. The kinetic modeling used in this study is based on the assumptions given by Moradi *et al.*, Birla *et al.*, and Zhang *et al.*[65−67]. The rate constant k can be obtained by fitting the experimental data of each ester concentration at various temperatures. And then, plotting ln k versus 1/T will give a straight line that Arrhenius plot displayed in Fig. 10. The observed rate constants of each fatty acid component of FAME were extracted by the pseudo-first-order assumption[67, 68] and then activation energies of each fatty acid of FAME were calculated based on Arrhenius equation as shown in Table 6. The order of the observed rate constants of the corresponding fatty acid-derived FAME at all temperatures was as the following; C18:2＞C18:1＞C16:0＞C18:3＞C18:0. The observed rate constants may correlate to the concentration of the corresponding fatty acid in the soybean oil. The activation energies of all FAMEs were in the range of 40-52 kJ/mol and the activation energy of the overall FAME was 46 kJ/mol. Kumar and Ali studied a pseudo first order kinetic model that was optimized conditions first order rate constant and activation energy was

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Table 5 Comparison of biodiesel production activity and properties of the synthesized biodiesel with other catalysts.

| Catalysts type | Transesterification condition | | | | Conversion (%) | Surface area (m$^2$/g)$^a$ | Ref. |
|---|---|---|---|---|---|---|---|
| | Molar ratio of Oil:Methanol | Time (h) | Catalyst amount (%wt) | Temp. (℃) | | | |
| KF/Ca(NO$_3$)$_2$ hydrogel (Catalyst **E**) | 1:15 | 15 min | 10 | 65 | 96.0 | 867.5 | this work |
| CaO-SnO$_2$ | 1:12 | 6 | 8 | 70 | 89.3 | N.A. | 59 |
| CaO-MoO$_3$-SBA-15 | 1:50 | 50 | 6 | 65 | 83.2 | N.A. | 60 |
| SBA-15 with 1,3-dicyclohexyl-2-octylguanidine | 1:15 | 15 | 8 | 65 | 92.6 | 267 | 61 |
| SBA-15-pr-NR$_3$OH | 1:12 | 30 min | 2.5 | 65 | 99.4 | 271 | 62 |

N.A. = Not available,
$^a$ Determined by BET method



**Fig. 8** Reuse of the two-step catalyst **E** for the biodiesel production（reaction conditions: 65℃ for 1 h with methanol/oil molar ratio 15:1 and a catalyst loading of 10 wt％）.

found 54 kJ/mol for nanocrystalline K–CaO catalyst by the transesterification[69]. Activation energies calculated by other reports were also in the range of 27 – 100 kJ/mol for transesterification of vegetable oil[70-73].

## 4 Conclusions

Novel catalysts were developed based on the sequential additions of KF and Ca(NO$_3$)$_2$ into the hydrogel upon microwave irradiation and then calcination at 800℃. The solid base KF/Ca(NO$_3$)$_2$ hydrogel can be used for biodiesel production with yield of more than 96％. The best catalyst of this preparation was the two-step catalyst, **E**, （KF 2.5 mol/dm$^3$/Ca(NO$_3$)$_2$ 2.5 mol/dm$^3$）. The optimum condition of transesterification reaction was as follows; 10％ catalyst amount, 15:1 methanol/oil molar ratio and 30 minutes for reaction time. BET analysis showed the high surface area of 867.5 m$^2$/g and crystal KCaF$_3$ from XRD results which increase catalytic activity. The high specific surface area favored to contact between catalyst and substrates, which improved efficiency of transesterification reaction. The elimination of the hydrogel template produced the high surface area materials which may be useful for the synthesis of other materials to increase the surface area. The prepared catalysts showed the mixed properties of homogeneous and heterogeneous catalysts which could be improved in future by the optimization of the components in the incorporations by microwave irradiation and the temperature of the calcination. The improvement of biodiesel yield may be carried out in a closed system at higher temperature for the development of commercial catalysts.

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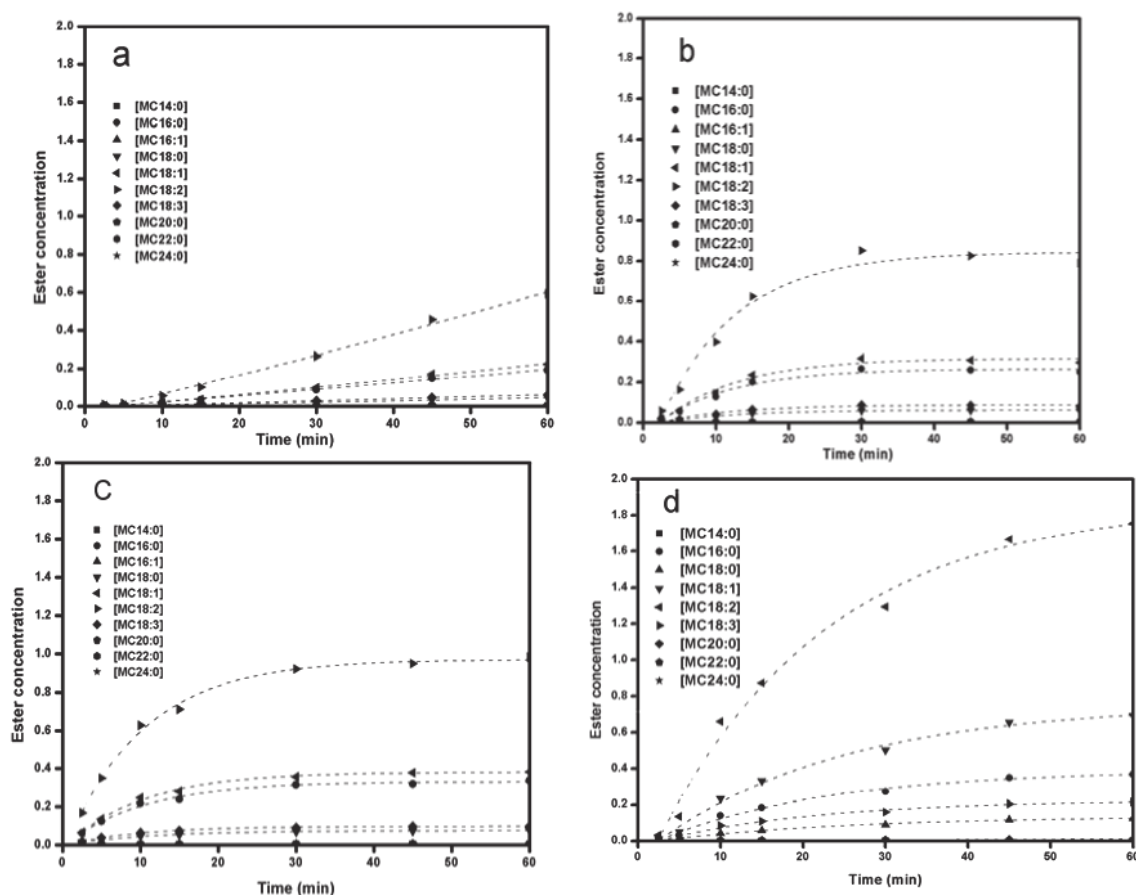4) Mardhiah, H.H.; Ong, H.C.; Masjuki, H.H.; Lim, S.; Lee,

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**Fig. 9** Ester concentrations of the two-step catalyst **E** at each temperature monitored by Gas Chromatography（a. 35℃, b. 45℃, c. 55℃ and d. 65℃）.

**Table 6** Rate constant and activity energy of the two-step catalyst **E** of each fatty acid methyl ester（FAME）.

| FAME | Observed Rate Constant (s$^{-1}$) | | | | Activation Energy (kJ/mol) |
|---|---|---|---|---|---|
| | 35 ℃ | 45 ℃ | 55 ℃ | 65 ℃ | |
| C16:0 | $5.4 \times 10^{-5}$ | $23 \times 10^{-5}$ | $31 \times 10^{-5}$ | $21 \times 10^{-5}$ | 40 |
| C18:0 | $1.2 \times 10^{-5}$ | $5.2 \times 10^{-5}$ | $6.9 \times 10^{-5}$ | $6.0 \times 10^{-5}$ | 44 |
| C18:1 | $6.2 \times 10^{-5}$ | $25 \times 10^{-5}$ | $39 \times 10^{-5}$ | $31 \times 10^{-5}$ | 46 |
| C18:2 | $16 \times 10^{-5}$ | $70 \times 10^{-5}$ | $90 \times 10^{-5}$ | $90 \times 10^{-5}$ | 47 |
| C18:3 | $1.7 \times 10^{-5}$ | $7.0 \times 10^{-5}$ | $9.3 \times 10^{-5}$ | $11 \times 10^{-5}$ | 52 |
| Overall | $38 \times 10^{-5}$ | $15 \times 10^{-4}$ | $21 \times 10^{-4}$ | $19 \times 10^{-4}$ | 46 |

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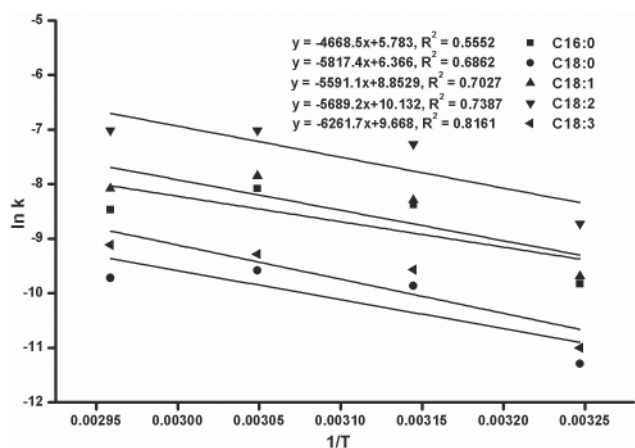
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$$y = -4668.5x+5.783, R^2 = 0.5552 \quad \blacksquare \quad C16:0$$
$$y = -5817.4x+6.366, R^2 = 0.6862 \quad \bullet \quad C18:0$$
$$y = -5591.1x+8.8529, R^2 = 0.7027 \quad \blacktriangle \quad C18:1$$
$$y = -5689.2x+10.132, R^2 = 0.7387 \quad \blacktriangledown \quad C18:2$$
$$y = -6261.7x+9.668, R^2 = 0.8161 \quad \blacktriangleleft \quad C18:3$$

**Fig. 10** Arrhenius plots of the two-step catalyst **E** at each fatty acid of FAME.

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