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A recyclable solid catalyst of KF/Ca-Mg-Al-O using for biodiesel production from jatropha seed oil: preparation, characterization, and methanolysis process optimization

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Abstract

A recyclable heterogeneous KF/Ca-Mg-Al-O catalyst was prepared by co-precipitation and calcination processes. The characteristics of the catalyst were investigated using FTIR, XRD, TG-DTG and SEM. Response surface methodology was utilized to obtain the best most extreme biodiesel production yield. The ideal biodiesel production conditions were: the amount of catalyst was 3 wt%; the reaction temperature was 65 °C; the alcohol oil molar ratio 9.8:1, the reaction time was 3.5 h. Under these amended conditions, the average biodiesel yield was 95.19%, which is well in close concurrence with the worth anticipated by the model. The repeatability of catalysts was studied. After using the catalyst seven times, the catalytic efficiency was only reduced by 2.7%. These results indicate that the catalyst has good catalytic efficiency and is recyclable.

1. Introduction

At present, the available petrochemical resources worldwide are decreasing every day. With the development of economy and society, the demand for energy is increasing. Petrochemical resources are gradually decreasing, and the use of fossil energy will cause emissions of toxic pollutants and carcinogens (Arunugam and Ponnusami 2019). However, biomass energy has the advantages of easy production and little pollution. As an important biomass energy source, biodiesel has received widespread attention (Quah et al 2019, Gohain et al 2020). At present, the preparation of biodiesel primarily includes physical method and chemical method (Yaakob et al 2013). The physical method includes a direct mixing method and a microemulsification method (Ayodeji et al 2018). The direct mixing method is simple to prepare, but the quality of biodiesel is not high, and carbon deposition can easily occur during combustion (Marwaha et al 2019). The micro-emulsion method has the disadvantages of poor stability and unstable storage process. Chemical methods primarily include high-temperature thermal cracking and transesterification. Although the high-temperature cracking method has a simple preparation process, the reaction process requires a reactor and consumes more energy (Lani et al 2019, Pandit and Fulekar 2019). Transesterification is a preparation method with good catalytic effects, mild preparation conditions, and high-quality biodiesel (Viriya-empikul et al 2010). Biodiesel is produced through transesterification with methanol or ethanol (Roschat et al 2016).

Transesterification focuses on the development of catalysts. The main research areas are enzyme catalysts, homogeneous catalysts, and solid catalysts. Enzyme catalysts are expensive and susceptible to deactivation (Fernandez et al 2017), which lead to excessive total cost of producing biodiesel and low catalytic efficiency. Homogeneous catalysts are difficult to separate, and they can easily contaminate the product (Mohadesi et al 2019). Solid catalysts have attracted considerable attention because of their high activity and easy separation. Solid catalysts are divided into solid acid catalysts and solid-base catalysts (Yaşar 2019). However, the solid acid
catalyst will corrode the reaction device and the pipeline during the reaction, and the equipment maintenance cost will increase (Shi et al. 2018, Vadery et al. 2019, Zhang et al. 2020). Common solid-base catalysts can be easily deactivated during storage, and they have high requirements for feedstock oil (Du et al. 2019) and easy saponification during the reaction (Joshi et al. 2016), which will affect the quality of biodiesel and cause environmental pollution (Abukhadra et al. 2019a). Therefore, this paper aims to study a supported solid-base catalyst to overcome the shortcomings of the original solid catalyst.

One of the key issues of this experiment is to study the carrier of supported solid-base catalysts (Ho et al. 2012, Mohadesi et al. 2018, Vardast et al. 2019, Abukhadra et al. 2019b). Metal oxides are widely used as catalyst carriers, but achieving the differences in acid value and saponification value of different raw materials is difficult when using a single metal oxide as a catalyst carrier (Ye et al. 2018, Corroa et al. 2019, Junior et al. 2019, Yusuff and Owolabi 2019). Larger cases still maintain high catalytic capabilities. The use of composite metal oxides as catalyst supports can improve the adaptability of the catalyst to different raw materials.

Composite metal oxides, such as Ca-Al-O, Mg-Al-O, and Zn-Al-O, have been used as biodiesel catalysts, and their catalytic activity sequence is as follows: Ca-Al-O > Mg-Al-O > Zn-Al-O (Rabie et al. 2019). When Ca-Al-O, Mg-Al-O, and Zn-Al-O are used as catalyst carriers, the order of catalyst’s ability to resist acid, water, and saponification is as follows: Zn-Al-O > Mg-Al-O > Ca-Al-O (Hsu et al. 2019, Kesserwan et al. 2020). As shown in the two sorts, the Mg-Al-O catalyst has a strong activity and fast catalytic reaction rate. Moreover, the Mg-Al-O catalyst has a certain degree of resistance to acid, water, and saponification, and it requires less raw materials.

The KF/Ca-Mg-Al-O catalyst uses Mg-Al-O as a catalyst carrier; thus, the catalyst has certain acid, water, and soap resistance. In addition, after the preparation of the Mg-Al-O carrier, it is modified with Ca(OH)$_2$, which not only enhances its acid, water, and soap resistance, but also increases the active site of KF when bound to the load (Pangestua et al. 2019).

This study focuses on biodiesel production from *Jatropha* seed oil using the KF/Ca-Mg-Al-O catalyst as a new catalyst through co-precipitation and calcination processes. The catalyst is characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM), and thermogravimetry and differential thermogravimetry (TG–DTG). The experiments show that the solid-base catalyst makes up for its disadvantages such as inactivation and saponification (Rosset and Perez-Lopez 2019). The RSM is applied to obtain the best conditions of biodiesel production, including the amount of catalyst, the reaction temperature; the alcohol oil molar ratio, the reaction time. The repeatability of catalysts was studied.

2. Materials and methods

2.1. Chemicals and raw materials

Market-purchased *Jatropha* seed oil, ammonia, methanol, aluminum chloride hexahydrate, magnesium chloride hexahydrate, potassium fluoride, and calcium hydroxide of AR grade were purchased from Wokai and Aladdin. Methyl oleate standard, methyl palmitate standard, methyl linoleate standard, and methyl linolenic acid standard of AR grade purchased from Maclean were drawn standard curves. Hammett indicators, namely, bromo thymol blue, phenolphthalein, and 2,4-dinitroaniline of AR grade purchased from Merck were used in this work.

2.2. Methods

2.2.1. Determination of physical and chemical indexes of *Jatropha* seed oil

According to GB/T5530-2005 and GB/T5534-1995, the acid value, saponification value, and molecular weight of the raw material oil were measured.

2.2.2. Catalyst preparation

Certain molar ratio of MgCl$_2$-6H$_2$O and AlCl$_3$-6H$_2$O was dissolved in 500 ml of deionized water, and 28% NH$_3$·H$_2$O was added to the solution until pH 10.0 and stirred at 70 °C for 2 h. Then, the solution was crystallized at 95 °C for 3 h. The liquid was filtered, and the filter residue was washed with deionized water until pH 7.0. The filter residue was dried and kept in a hot air oven at 105 °C for 12 h to obtain magnesium aluminum hydrotalcite. Magnesium aluminum hydrotalcite was calcined in a furnace up to 550 °C for 4 h to obtain Mg-Al-O. The Mg-Al-O was smashed into powder using a ball mill. 10.00 g of powder was immersed in 2% Ca(OH)$_2$ solution for 12 h using equal-volume impregnation. The solid was dried at 80 °C and calcined in a muffle furnace at 650 °C for 3 h to obtain the catalyst carrier Ca-Mg-Al-O.

10.00 g of Ca-Mg-Al-O was immersed in a certain concentration of KF solution for 12 h using equal-volume impregnation. The catalyst carrier was dried at 80 °C and calcined at a certain temperature for a certain period of time to obtain a biodiesel catalyst KF/Ca-Mg-Al-O.
The research content includes the following aspects: the molar ratio of magnesium to aluminum is 1:3, 1:2, 1:1, 2:1, 3:1, and 4:1; the amount of Ca is 0%, 1%, 2%, 3%, 4%, and 5%; the KF addition amounts are 10%, 15%, 20%, 25%, and 30%; the calcination temperatures are 400 °C, 500 °C, 600 °C, 700 °C, 800 °C, and 900 °C, respectively; calcination time is 2, 3, 4, 5, 6, and 7 h.

2.2.3. Biodiesel quantitative analysis
The content of fatty acid methyl ester was quantitatively analyzed by gas chromatography (Essamlali et al. 2019). The chromatographic conditions were as follows: flame ionization detector was used; the column was AE. FFAP (30 m × 0.25 mm × 0.25 μm); the inlet temperature was 260 °C; the injection volume was 1 μl, and the split ratio was 15:1. The temperature programming scheme was as follows: the initial temperature was maintained at 150 °C for 3 min, increased to 200 °C at 10 °C min⁻¹, and then increased to 250 °C for 5 min at 5 °C min⁻¹.

\[
\text{Yield} = \frac{\text{Actual amount of biodiesel}}{\text{Theoretical amount of biodiesel}} \times 100\% \quad (1)
\]

2.2.4. Catalyst characterization
XRD analysis was performed with Cu, Kα target, Ni filter, tube voltage of 20 kV, tube current of 20 mA, scanning speed of 0.1° s⁻¹, and scanning range of 10°–80°.

FT-IR analysis was conducted with a scanning range of 4000–400 cm⁻¹, instrument resolution of 4 cm⁻¹, and scanning 16 times. The infrared test sample was prepared by KBr tableting, and the sample was approximately 2% of the KBr mass.

TG–DTG analysis: The thermal change of the catalyst and catalyst carrier was studied at 30 °C, a termination temperature of 800 °C, and a heating rate of 10 °C min⁻¹. SEM analysis: Measurement was carried out under an electron acceleration voltage of 20 kV at room temperature. The catalyst was characterized by SEM to determine the particle size and surface structure.
2.2.5. Biodiesel production

The trans-esterification reaction was performed in three of them burn bottles (150 ml), equipped to a reflux condenser and a magnetic stirrer. Then, the preprocessed *jatropha* oil was first blended in with methanol in variable molar ratios (8:1-14:1), and afterward stacked into the reaction vessel with the addition of proper amount of KF/Ca-Mg-Al-O catalyst (1–7 wt %). Next, the reaction temperature was changed (40 °C–70 °C), and the reaction time was differed from 2.5 to 5 h to guarantee the appropriate transformation of triglycerides to unsaturated fatty acid methyl esters (FAMEs).

Then, the reaction mixture was cooled down and centrifugated. After centrifugation, crude biodiesel, glycerol and catalyst were used from top to bottom. The upper layer is dumped into the split funnel, adding purified water, fully shaken, static, layered, discharging the lower water layer, and repeating the above operation many times until the upper biodiesel is neutral. Anhydrous sodium sulfate was added to the washed biodiesel and centrifuged to obtain the biodiesel.

| Name                  | Unit               | Value  |
|-----------------------|--------------------|--------|
| Acid value            | mg KOH/g           | 7.68   |
| Saponification value  | mg KOH/g           | 184.56 |
| Water content         | %                  | 0.11   |
| Iodine value          | g/100 g            | 101.56 |
| Molecular weight      | g/mol              | 951.49 |

Table 2. Physical and chemical properties of *Jatropha* seed oil.

Figure 1. Effect of the molar ratio of magnesium to aluminum on FAMEs (reaction conditions: calcium content of 4%, KF load of 20%, calcination temperature of 600 °C, and calcination time of 3 h). (b) Effect of calcium content on FAMEs (reaction conditions: magnesium-to-aluminum molar ratio of 3:1, KF load of 20%, calcination temperature of 600 °C, and calcination time of 3 h). (c) Effect of KF load on FAMEs (reaction conditions: magnesium-to-aluminum molar ratio of 3:1, calcium content of 2%, calcination temperature of 600 °C, and calcination time of 3 h).
RSM is an statistical method that utilizes quantitative information from fitting test plan to decide and all the while tackle multivariate conditions. Hence, RSM is less difficult and less tedious than other methods (Yin et al 2011).

Central Composite Design (CCD) of RSM was applied to study the impact factors for biodiesel preparation. Based on the preliminary range of extraction variables, a four-level-three-factor CCD was adopted in this study. The independent variables $X_1, X_2, X_3, X_4$ represent the catalyst dosage (wt%), alcohol oil molar ratio (mol: mol), reaction temperature ($^\circ$C), reaction time (h), table 1 is design and results of CCD, the examination was done in a standard order. The conduct of the system was clarified by the next second degree polynomial equation:

$$y = \beta_0 + \sum_{i=1}^{4} \beta_i X_i + \sum_{i=1}^{4} \beta_{ii} X_i^2 + \sum_{i<j=2}^{4} \beta_{ij} X_i X_j$$

(2)

$y$ is the response function, $\beta_0$ is an intercept, $\beta_i, \beta_{ii}$ and $\beta_{ij}$ are the coefficients of the linear, quadratic and interactive terms, individually. And accordingly $X_i$ and $X_j$ address the coded free independent factors.

The fitted polynomial condition is communicated as surface plots to imagine the connection between the response and trial levels of each factor and to obtain the ideal conditions. Design-expert (Version8.0.6.1) software package was utilized to examine the trial information. P-values of less than 0.05 were viewed as genuinely critical.

3. Results and discussion

3.1. Physicochemical properties of raw oils and contents

Table 2 shows the acid value, saponification value, water content, iodine value, and molecular weight of Jatropha seed oil.

As shown in table 2, Jatropha seed oil has a molecular weight of 951.49 g mol$^{-1}$, water content of 0.11%, acid value of 7.68 mg KOH/g, and iodine value of 101.56 g/100 g. Jatropha seed oil has good fluidity.

Jatropha seed oil has a high acid value of 7.68 mg KOH/g. Considering that the catalyst used in the transesterification reaction is a solid-base catalyst, a high acid value is not conducive to the transesterification reaction. 20.0 g of Jatropha seed oil was collected and put into a separatory funnel. Then, 100 ml of methanol was added to the separatory funnel, and the mixture was shaken thoroughly. After five reciprocations, the acid value of Jatropha seed oil dropped to 0.84 mg KOH/g.

The fatty acid of Jatropha seed oil was methylated, and the fat methyl ester content of the selected Jatropha seed oil was analyzed by gas chromatography–mass spectrometry. Table 3 shows the fatty acid methyl ester.

3.2. Investigation of catalyst preparation conditions

3.2.1. Effect of the molar ratio of magnesium to aluminum on biodiesel yield

As shown in figure 1(a), the yield of biodiesel increases with the increase of the magnesium-to-aluminum molar ratio. When the ratio of magnesium to aluminum is 3:1, the yield of biodiesel is the largest. This might because that the basicity of MgO is stronger than that of Al$_2$O$_3$, the alkalinity of the whole catalyst is increased with the increase of magnesium to aluminum ratio, thereby its catalytic activity increased (Lawan et al 2020). On the other hand, the electronegativity of aluminum is stronger than that of magnesium. When magnesium ratio increases, the relative number of aluminum decreases, and the average electronegativity of the catalyst also decreases, the number of basic active sites in the catalyst increased with the increase of magnesium to aluminum ratio, and the conversion rate of biodiesel increased (Cheng 2011, Lawan et al 2020). When the molar ratio of magnesium to aluminum is 4:1, the alkaline enhancement of the whole catalyst is not evident and the biodiesel yield changed slightly. Gao et al reported that when the ratio of divalent cation to trivalent cation for the catalyst was high, too much divalent cation could hindered their combination with the trivalent cation to form the layer structure, and too much divalent cations were added and there were not enough trivalent cations to act with them (Gao et al 2010). Therefore, the selected magnesium-to-aluminum molar ratio is 3:1.

### Table 3. Fatty acid methyl ester composition of Jatropha seed oil.

| Ingredient        | Formula      | % (w/w) |
|-------------------|--------------|---------|
| Methyl palmitate  | C_{16}H_{32}O_{2} | 15.5    |
| Methyl oleate     | C_{18}H_{34}O_{2} | 50.5    |
| Methyl linoleate  | C_{18}H_{32}O_{2} | 18.7    |
| Methyl linolenate | C_{18}H_{30}O_{2} | 5.3     |

Methyl palmitate C$_{16}$H$_{32}$O$_{2}$ 15.5 
Methyl oleate C$_{18}$H$_{34}$O$_{2}$ 50.5 
Methyl linoleate C$_{18}$H$_{32}$O$_{2}$ 18.7 
Methyl linolenate C$_{18}$H$_{30}$O$_{2}$ 5.3
3.2.2. Effect of calcium content on biodiesel yield
As shown in figure 1 (b), biodiesel yield increased when calcium content was less than 2% and decreased when calcium content was higher than 2%. When the calcium content was 2%, the biodiesel yield was the highest. When the calcium content was higher than 2%, the biodiesel yield decreased with the increase of calcium content. It suggests that Ca is essential in the creation of the active sites for transesterification. The Ca impregnated on the surface of the Mg-Al HT created active sites for the reaction to occur (Dahdah et al). Castro et al reported that Ca content could affects the amount of base sites/base site strength, and the physical structure of the catalysts (Castro et al 2014). On the other hand, when the Ca²⁺ content increased, more Al³⁺ combined with it and partly destroyed the layer structure, the Mg²⁺ relative molar ratio decreased instantaneously, and then less KMgF₃ was formed (Gao et al 2010).

3.2.3. Effect of KF load on biodiesel yield
As shown in figure 1 (c), the activity of the catalyst increased with the increase of the KF load. When the KF load reached 25%, the biodiesel yield was the highest. When the KF load was further increased, the biodiesel yield decreased slowly probably because 25% KF has already occupied all the surface-active sites, and further increasing KF could not be combined with the active site. Moreover, the catalytic activity per unit was lowered during the preparation of biodiesel. Thus, KF load of 25% was selected.

3.2.4. Effect of calcination time on biodiesel yield
As shown in figure 2(a), the biodiesel yield increases with the increase of calcination time. When the calcination time was 4 h, the biodiesel yield was the highest, but the catalytic effect was almost unchanged when longer than 4 h probably because the catalytically active structure has formed on the surface of the catalyst, and there is little change with the extension of time. Therefore, 4 h was selected as the calcination time.

3.2.5. Effect of calcination temperature on biodiesel yield
As shown in figure 2(b), the activity of the catalyst increases as the calcination temperature increases. When the calcination temperature reaches 700 °C, the biodiesel yield was the highest, which may be due to the change of the pore structure of the catalyst surface and the occurrence of the calcination temperature. Upon chemical reaction, a new composite metal oxide is formed on the surface. However, the catalytic effect continuously increases, which may be due to the fact that the temperature is too high to destroy the active structure of the catalyst; thus, the catalytic effect is lowered. Therefore, 700 °C was selected as the calcination temperature of the catalyst.

3.3. Catalyst characterization
3.3.1. Basic strength characterization
The catalyst prepared under optimized conditions was subjected to color reaction with bromo thymol blue (pKₐ = 7.2), phenolphthalein (pKₐ = 9.8), and 2,4-dinitroaniline (pKₐ = 15.0). It can make bromo thymol blue and
phenolphthalein alkaline color, but it cannot make a 2,4-dinitroaniline alkaline color. Therefore, the basic strength of the catalyst was 9.8–15.0.

3.3.2. XRD analysis
As shown in figure 3, the difference among the diffraction peaks of Mg-Al-O, CaO, KF, and KF/Ca-Mg-Al-O solid-base catalysts was at diffraction angles of 10° to 80°. After modification with Ca, the corresponding diffraction peak of Mg-Al-O at 65° and the broad peak corresponding to 37° disappear, and a new diffraction peak appears.
peak is formed at approximately 55°, which proves that CaO is not simply dispersed on the surface of the KF/Ca-Mg-Al-O catalyst, and forming a new composite metal oxide Ca-Mg-Al-O as a catalyst carrier by calcination at a high temperature and Mg-Al-O is possible. Compared with KF and KF/Ca-Mg-Al-O catalysts, the characteristic diffraction peaks of KF at 34° and 46° disappeared, which proved that KF was not loaded onto the surface of the catalyst carrier. This may be that after calcination at high temperature, new compounds such as KCaF3 were formed. The following experimental results of FI-IR verified this conclusion.

3.3.3. FT-IR analysis
As shown in figure 4(b), compared with the infrared spectrum of uncalcined and calcined Mg-Al-O, the -OH peak of 3500 cm\(^{-1}\) was significantly weakened after calcination and appeared at 1700 and 1400 cm\(^{-1}\) before calcination. The sharp peak, stretching vibration peak of Mg-O at 1700 cm\(^{-1}\), and the stretching vibration peak of Al-O at 1400 cm\(^{-1}\) almost disappeared after calcination. In addition, the vibration peak of Al-O-Mg was formed at 694 and 578 cm\(^{-1}\); thus, a composite metal oxide Mg-Al-O was formed.

As shown in figure 4(c), the infrared pattern of Ca-Mg-Al-O before and after calcination was compared. Considering that Ca(OH)\(_2\) was used for modification, the bound water was reduced after calcination, resulting in a significant decrease in the -OH stretching vibration peak of the bound water (3500 cm\(^{-1}\)). The peak appearing at 3650 cm\(^{-1}\) after calcination was the stretching vibration peak of Ca-O. Comparing Ca-Mg-Al-O (uncalcined) with Mg-Al-O (calcined) in figure 4(b), significant Ca-O-Mg and Ca-O-Al stretching vibration peaks were observed at 1640 and 1460 cm\(^{-1}\). After calcination, the stretching vibration peak of Ca-O-Mg at 1650 cm\(^{-1}\) disappeared, and a single absorption peak was formed at 1490 cm\(^{-1}\), which was presumed to be a metal oxide formed by the combination of three metals, namely, Ca, Mg, and Al.

Comparing the infrared spectra before and after calcination of KF/Ca-Mg-Al-O, two new absorption peaks are formed at 1480 and 1380 cm\(^{-1}\) (figure 4(d)). Therefore, a stretching vibration peak is estimated to be Ca-F-K, and KCaF\(_3\) may be formed.

In the infrared spectra of KF and CaO, the peak between 3750 and 3600 cm\(^{-1}\) is a stretching vibration peak belonging to Ca-O, and the infrared spectrum after calcination from KF and KF/Ca-Mg-Al-O shows the disappearance of the characteristic peak of KF from 1750 cm\(^{-1}\) to 1650 cm\(^{-1}\) and the weakening of the characteristic peak from 1850 cm\(^{-1}\) to 1800 cm\(^{-1}\). The newly emerging peaks at 3500 and 750 cm\(^{-1}\) prove that KF is not only loaded onto the surface of the body, but also formed by calcination with the carrier at a high temperature.

By comparing the infrared spectra of Mg-Al-O (calcined) and Mg-Al-Ca-O (calcined), a new compound (Ca-Mg-Al) may be formed after modification of Ca at 1450 cm\(^{-1}\). This finding is also demonstrated by the XRD
pattern in figure 3. The double peak at 1450 cm\(^{-1}\) after calcination of KF/Ca-Mg-Al-O (figure 4(d)) demonstrates that KF binds to the carrier after calcination to form a new compound.

3.3.4. TG–DTG analysis

As shown in figure 5(a), Mg-Al-O has four distinct thermogravimetric stages at 85 °C–105 °C, 135 °C–150 °C, 220 °C–260 °C, and 450 °C–500 °C. 85 °C–105 °C was the weight loss caused by the removal of adsorbed water and surface-adsorbed carbon dioxide, and the weight loss rate was approximately 4%. 135 °C–150 °C was the weight loss caused by the removal of adsorbed water in the internal void structure of Mg-Al-O, and the weight loss rate was approximately 2.3%. The weight loss peak of 220 °C–260 °C corresponded to the removal of bound water between internal voids, and the weight loss rate was approximately 7.1%. The weight loss peak at 450 °C–500 °C was due to dehydroxylation or anion between the magnesium–aluminum hydroxylate layers, and the weight loss rate was approximately 18.3%. When the temperature was higher than 500 °C, the mass change of Mg-Al-O was small.

As shown in figure 5(a), the calcination temperature of Mg-Al-O should not be lower than 500 °C, but too high temperature might destroy the surface structure of Mg-Al-O. Moreover, the voids might collapse, and Mg-Al-O might be agglomerated. Therefore, the selected optimum calcination temperature was 600 °C.

As shown in figure 5(b), Ca-Mg-Al-O has three distinct stages of thermal weight loss at 85 °C–125 °C, 320 °C–400 °C, and 630 °C–680 °C. 85 °C–125 °C was the weight loss caused by the removal of adsorbed water and surface-adsorbed carbon dioxide on the surface, and the weight loss rate was approximately 2.5%. The weight loss peak at 320 °C–400 °C was due to the removal of bound water in the internal void of Ca-Mg-Al-O and the removal of hydroxide in the modified Ca(OH)\(_2\), and the weight loss rate was approximately 3%. The weight loss peak of 630 °C–680 °C may be the weight loss caused by CaO and Mg-Al-O forming a new composite metal oxide of Ca-Mg-Al-O, and the weight loss rate was approximately 1.8%. Therefore, Ca-Mg-Al-O may be formed similar to that obtained in figure 4. The mass of the carrier Ca-Mg-Al-O slightly increases when continuously increasing the temperature.

As shown in figure 5(b), the calcination temperature was lower than 680 °C to form a catalyst carrier. If the calcination temperature is too high, then the surface structure of Ca-Mg-Al-O may be destroyed; the voids may collapse, and Ca-Mg-Al-O may be agglomerated, which will reduce the loading sites of KF and decrease the catalytic efficiency of the final catalyst. Therefore, the selected optimum calcination temperature was 700 °C.

As shown in figure 5(c), KF/Ca-Mg-Al-O has four distinct thermogravimetric stages at 65 °C–115 °C, 300 °C–350 °C, 360 °C–420 °C, and 600 °C–670 °C. 65 °C–115 °C is the weight loss caused by the removal of adsorbed water and surface-adsorbed carbon dioxide on the surface, and the weight loss rate is approximately 6%. The weight loss peak at 300 °C–350 °C is the removal of some of the hydroxyl groups hydrated by Mg-Al-O during impregnation, and the weight loss rate is approximately 4.2%. The weight loss peak of 360 °C–430 °C may be the removal of the hydroxyl group of Ca(OH)\(_2\) formed by CaO during impregnation, and the weight loss rate is approximately 1.6%. The weight loss peak at 600 °C–670 °C, the possible loading of KF, and the new compound formed by calcination of the catalyst carrier were considered as the active components of the catalyst. This hypothesis is consistent with the conclusions obtained in figure 3.
As shown in figure 5(c), when forming a KF/Ca-Mg-Al-O catalyst, the calcination temperature should not be lower than 670 °C. If the calcination temperature is too high, then the surface structure of the catalyst may be destroyed; the voids may collapse, and the catalyst may agglomerate. The active site leading to the catalytic reaction is reduced, and the catalytic effect of the final catalyst is lowered. Therefore, the selected optimum calcination temperature was 700 °C.

3.3.5. SEM analysis
As shown in figure 6(a), the surface of the calcined carrier Ca-Mg-Al-O at 700 °C has many fine granular structures; the entire surface is relatively flat, and the overall structure is relatively regular.

As shown in figure 6(b), the surface of the catalyst KF/Ca-Mg-Al-O after loading KF has a large particle structure, and the lamellar structure appears on the surface of the particle probably because of the loading of KF. This finding can also explain the decrease in the specific surface area of the catalyst after loading. Moreover, a pore-like structure appears on the solid surface, which allows the catalyst to combine with the reactants and provide a good catalytic effect. Furthermore, an interaction is found between the loaded KF and carrier, which is not simply carried on the surface.

3.4. Effective parameters of biodiesel production
3.4.1. Effect of KF/Ca-Mg-Al-O catalyst dosage on FAMEs yield
As shown in figure 7(a). When the catalyst dosage is less than 3 wt%, the yield of FAMEs increased, at the catalyst dosage of 3 wt%, the biodiesel yield was the highest, continue to increase the catalyst dosage, FAMEs yield did
not change significantly. The reason is that when the amount of catalyst is less than 3%, increasing the catalyst amount will increase the alkalinity in the reaction system, the alkali activity center of the reaction increases with the increase of the catalyst (Lawan et al. 2020), plays a role in promoting the reaction, and increases the yield of FAMEs. When the catalyst continues to increase, the whole reaction system has been saturated, and thus the FAMEs yield does not change significantly. So the optimal amount of the catalyst selected is 3 wt%.

3.4.2. Effect of methanol/oil molar ratio on FAMEs yield
As shown in figure 7(b), at the alcohol oil molar ratio below 10:1, the FAMEs yield ratio increases with the alcohol oil mole ratio, the peak of the FAMEs yield appears at 10:1, and at the alcohol oil molar ratio above 10:1, the FAMEs yield decreases with the alcohol oil molar ratio above 10:1. The reason for the rising stage is that increasing the reactant methanol can promote the positive movement of the ester exchange reaction balance and promote the production of FAMEs (Dahdah et al. 2020). Therefore, the FAMEs yield increases with the alcohol oil molar ratio. However, when it continues to increase the methanol consumption, on the one hand, the concentration of the dilution catalyst in the system will be not conducive to the movement of the reaction to be positive, and on the other hand, it will reduce the concentration of the pretreatment mad seed oil in the reaction system. Moreover, excess methanol is dissolved in biodiesel, increasing the cost of separation and recovery, and, therefore, 10:1 was chosen as the best alcohol oil molar ratio.

3.4.3. Effect of reaction temperature on FAMEs yield
As shown in figure 7(c), the yield of FAMEs increases with the temperature at the reaction temperature below 65 °C, the highest biodiesel yield at 65 °C, and at the reaction temperature above 65 °C, the FAMEs yield decreases with the reaction temperature. The reason is that as the temperature increases, the molecular movement in the reaction system accelerates, and the biodiesel yield increases with the reaction temperature. On the one hand, continuing to increase the temperature, the rapid reduction of methanol in the liquid phase leads to an increase in the volatilization amount of methanol during the reaction process, which is not conducive to the positive movement of the ester exchange reaction balance, aggravates the reverse reaction degree, and reduces the yield rate of FAMEs; on the other hand, the transesterification is chemical reaction controlled in the low temperature range as the energy provided for the reactant molecules to generate transesterification is inadequate. At the higher temperature, the transesterification is more easily generated and the higher molecular activity impels the equilibrium towards the products. At the same time, the mass transfer resistances between the heterogeneous catalyst and the liquid reactants become weak due to the reduced viscosity (Niu et al. 2018, Niu et al. 2020). So determining the temperature of 65 °C is the optimal reaction temperature.

3.4.4. Effect of reaction time on FAMEs yield
The transesterification prompted for the methyl esters production with a rapid rate, where the biodiesel yield is markedly, increased through prolonging the transesterification duration (Ganesan et al. 2019). Figure 7(d) shows that with longer than 3.5 h, the FAMEs yield increased at less than 3.5 h, with the highest biodiesel production at 3.5 h, and the FAMEs yield did not change significantly. The reason is that when this reaction is less than 3.5 h, the reaction is still moving forward. No equilibrium, and when reached 3.5 h, the reaction of preparing biodiesel has reached a dynamic equilibrium, continues to extend the reaction time, and will not have much impact on the reaction system. Therefore, 3.5 h was chosen as the best value of the reaction time.

3.4.5. Optimization of biodiesel production by RSM
3.4.5.1. Statistical analysis and the model fitting
Response surface optimization is more favorable than the traditional single parameter optimization in that it saves time, space and unrefined material (You et al. 2014). There were a sum of 29 runs for enhancing the four individual parameters in the CCD, the experimental conditions and biodiesel yield according to the factorial design was displayed in table 1. The experimental results showed that the biodiesel yield was 90.6% to 95.18%; the results were predicted using Design software and the predicted best conditions for biodiesel production is catalyst dosage of 3.01 wt%, alcohol oil molar ratio of 9.79:1, reaction temperature of 65.84 °C, reaction time of 3.52 h, at this time, the FAMEs yield was 95.21%. The outcomes were fitted with a second order polynomial equation. The values of equation regression coefficients were determined, the response variable and the test factors are connected by the following second-order polynomial equation (3):

\[
Y = 95.11 + 0.082X_1 - 0.19X_2 + 0.16X_3 + 0.17X_4 - 0.42X_2X_3 - 0.23X_1X_3 \\
+ 0.11X_2X_4 + 0.52X_1X_5 + 0.022X_3X_4 + 0.031X_1X_4 - 2.56X_3^2 - 1.7X_4^2 \\
- 1.41X_1^2 - 1.01X_2^2 
\]

(3)
The statistical significance of the polynomial regression equation was checked by F-test and p-value, and the analysis of variance (ANOVA) for the response surface quadratic equation model was displayed in Table 4. The determination coefficient ($R^2 = 0.9874$), displayed by ANOVA of the quadratic regression equation model, showing that the regression equation model was effective for prediction for expectation inside the scope of test factors. The linear coefficients ($X_2, X_3, X_4$), a quadratic term coefficient ($X_1^2, X_2^2, X_3^2, X_4^2$) and the interaction coefficient ($X_1X_2, X_2X_3, X_3X_4$) were seen as exceptionally critical ($p < 0.04$).

### 3.4.5.2. Optimization of the variable parameters

The RSM numerical approach was used to predict the optimum conditions in biodiesel production. Response surfaces were plotted by utilizing Design expert (version 8.0.6.1) programming to concentrate on the impacts of factors and their interactions on FAMEs yield. The full model filled equation (3) was made three dimensional graph to anticipate the connections between the dependent variables and the independent variables (Yin et al 2011).

![Figure 8. (a) Response surface of interaction between catalyst dosage and alcohol-to-oil ratio on FAMEs yield. (b) Response surface of interaction between catalyst dosage and reaction temperature on FAMEs yield. (c) Response surface of interaction between catalyst dosage and reaction time on FAMEs yield. (d) Response surface of interaction between alcohol-to-oil ratio and reaction temperature on FAMEs yield. (e) Response surface of interaction between alcohol-to-oil ratio and reaction time on FAMEs yield. (f) Response surface of interaction between reaction temperature and reaction time on FAMEs yield.](image)

**Table 4. ANOVA of response surface model.**

| Factor   | SS  | df | MS   | F值   | P值   |
|----------|-----|----|------|-------|-------|
| model    | 57.39 | 14 | 4.10 | 56.06 | <0.0001  |
| $X_1$    | 1.8  | 1  | 1.8  | 24.64 | 0.0002 |
| $X_2$    | 4.07 | 1  | 4.07 | 55.68 | <0.0001 |
| $X_3$    | 1.29 | 1  | 1.29 | 17.6  | 0.0009 |
| $X_4$    | 5.14 | 1  | 5.14 | 70.22 | <0.0001 |
| $X_1X_2$ | 0.01 | 1  | 0.01 | 0.14  | 0.7171 |
| $X_1X_3$ | 2.67 | 1  | 2.67 | 36.55 | <0.0001 |
| $X_1X_4$ | 0.26 | 1  | 0.26 | 3.56  | 0.0802 |
| $X_2X_3$ | 1.93 | 1  | 1.93 | 26.42 | 0.0002 |
| $X_3X_4$ | 0.0033 | 1 | 0.0033 | 0.041 | 0.8418 |
| $X_1^2$  | 0.023 | 1 | 0.023 | 0.31  | 0.5879 |
| $X_2^2$  | 0.31  | 1  | 0.31  | 4.26  | 0.0581 |
| $X_3^2$  | 9.13  | 1  | 9.13  | 124.89| <0.0001 |
| $X_4^2$  | 33.84 | 1  | 33.84 | 462.74| <0.0001 |
| Residual | 1.02 | 14 | 0.073 |       |       |
| Lack of Fit | 0.75 | 10 | 0.075 | 1.09  | 0.5090 |
| Pure Error | 0.27 | 4  | 0.069 |       |       |
| Cor Total | 58.42 | 28 |       |       |       |
The results of FAMEs yield impacted by catalyst dosage, alcohol oil molar ratio, reaction temperature, reaction time. These kinds of plots show impacts of two variables on the response at a time and the other variables was kept at level zero. As can be seen in figure 8(a), the FAMEs yield is greatly affected by the catalyst dosage and alcohol oil molar ratio, and the overall trend is rising first and then decreasing, indicating that the best value makes the highest FAME yield. Moreover, it can be seen that the catalyst dosage and alcohol oil molar ratio strongly interact from figure 8(a). Figures 8(b) and (c) is similar to the surface situation reflected in figure 8(a), so that the catalyst dosage strongly interacts with both the reaction temperature and the reaction time, and both have the optimal value of the FAME yield. In figure 8(d), the overall smoothness of the surface from the alcohol molar ratio shows that the alcohol molar ratio has less impact on FAMEs yield, while the FAMEs yield changes rapidly in the reaction temperature direction and has greater impact on FAME yield, with the best value interaction value. Figures 8(e) and (f) reflect a similar situation to figure 8(c), with large surface changes in the direction of the reaction time, indicating that the reflected reaction time factors have a strong impact on the experimental results.

In a word, the above four experimental factors have an interaction on FAMEs yield, but the relationship between the factors from the contour chart is: the weakest catalyst dosage, reaction temperature, reaction time, and the impact of alcohol oil mole ratio on FAMEs yield.

3.4.5.3. Verification of predictive model
The conditions for optimum FAMEs yield was obtained from the regression model equation. The suitability of the model equation for predicting the optimum response values was tested by using series of five experiments. The predicted best conditions for biodiesel production is catalyst dosage of 5.5 wt%, alcohol oil molar ratio of 8.84:1, reaction temperature of 54.27 °C, reaction time of 3.89 h, at this time, the FAMEs yield was 95.34%.

Considering practical consideration, the conditions for biodiesel preparation of catalyst dosage were selected as 3 wt%, alcohol oil molar ratio 9.8:1, reaction temperature 66 °C, reaction time is 3.5 h, three experiments, the average yield of FAME of 95.19% is close to the predicted theoretical value of 95.21%, indicating that the model can accurately describe the actual situation. It is shown that the model can be applied to a magnetic concave earth catalyst for biodiesel preparation.

3.4.6. Application and repeatability of catalysts
The biodiesel prepared by transesterification using KF/Ca-Mg-Al-O as catalyst was studied. The molar ratio of alcohol to oil was 10:1; the amount of catalyst was 3%; the reaction temperature was 65 °C, and the reaction time was 3.5 h. The rate reached 94.3%.
The KF/Ca-Mg-Al-O catalyst was centrifuged, dried, and used multiple times to study its recyclability. The relationship between the number of reuses and biodiesel yield was observed. The experimental results are shown in figure 9.

As shown in figure 9, the biodiesel yield reduces only by 2.9% within seven catalyst reuses. After the adsorption of glycerol, the active site covers and blocks the pore structure of the KF/Ca-Mg-Al-O catalyst, which is not conducive to the next step of repeated use. Simultaneously, the active component of the catalyst loading reduces during the catalytic reaction, resulting in a decrease in catalytic activity.

4. Conclusions

In this experiment, a co-precipitation method and an equal-volume impregnation method were used to prepare a supported solid-base catalyst (KF/Ca-Mg-Al-O). The characteristics of the catalyst were investigated using FTIR, XRD, TG-DTG and SEM. RSM was utilized to get the best maximum biodiesel production. The 3D response surface plot got from the mathematical equation were applied to decide the ideal conditions. After using the catalyst seven times, the catalytic efficiency was only reduced by 2.7%. These results indicate that the catalyst has good catalytic efficiency, and suggests its potential for industrial applications.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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