



CE/KAOLIN CLAY AS AN ACTIVE CATALYST FOR FATTY ACID METHYL ESTERS PRODUCTION FROM COTTONSEED OIL IN A NEW INTEGRATED APPARATUS

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Abstract – An efficient solid acid catalyst (Ce/Kaolin clay) was prepared and investigated for transesterification of cottonseed oil to fatty acid methyl esters (FAME). The catalysts were characterized by XRD, BET, and NH₃-TPD measurements. A new integrated apparatus for extraction and transesterification of cottonseed oil was developed. The effects of cerium loading, catalyst calcination temperature, methanol flow rate, reaction temperature, reaction time, and catalyst amount were also investigated. The results indicated that the Ce/Kaolin clay showed high catalytic activity under the calcination temperature of 700 °C and cerium loading of 0.05 g/g. The optimum transesterification reaction conditions were as follows: methanol flow rate 4.0 mL/min, reaction temperature 60 °C, reaction time 3 h, and catalyst amount 15 g. Under these conditions, the yield of FAME was up to 91%. The catalytic activity of Ce/Kaolin clay still remained high after 4 times of repeated use. The results indicated that the Ce/Kaolin clay catalysts had a good potential for use in the large-scale production of FAME.

Keywords: Ce/Kaolin clay, integrated apparatus, transesterification, fatty acid methyl esters, cottonseed oil

INTRODUCTION

Due to the limited fossil fuel resources and increasing environmental problems, great efforts have been dedicated to developing renewable biomass and biofuels. In this context, fatty acid methyl esters (FAME) are considered as a promising substitute to traditional fossil fuels due to their renewable, environmentally benign, and carbon neutral characteristics (Kumar and Ali, 2014). FAME are generally produced from vegetable oils or animal fats. In the industrial transesterification process, base or acid catalysts such as sodium hydroxide (NaOH) (Semwal et al., 2011) and sulfuric acid (H₂SO₄) (Moradi et al., 2013) are used as the catalysts. The advantage of this technology is that high FAME yield can be obtained under moderate reaction conditions. However, homogeneous catalysts show many

drawbacks, such as difficulty to be reused, complicated process of post treatment, and serious environmental problems (Guo et al., 2013).

In contrast, heterogeneous catalysts exhibit many advantages, such as environmentally friendly, easy separation, and simple post treatments. The transesterification reaction can be conducted over solid acid or base catalyst. Although the transesterification rate over the base catalysts is faster, the activity of base sites is reduced after neutralization with fatty acid during the alkaline-metal-hydroxide-catalyzed transesterification. Furthermore, the water and the fatty acids can form soap. Therefore, we investigated the transesterification reaction of cottonseed oil over solid acid catalysts.

Kaolin clay is a cheap and versatile raw material which can be found in numerous geographical locations and has

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been used successfully in the synthesis of mesoporous aluminosilicates (Liu et al., 2004) and various microporous zeolite frameworks (Belviso et al., 2013; Holmes et al., 2012; Holmes et al., 2011; Kovo et al., 2009; Shen et al., 2009). However, raw Kaolin clay has almost no acidity. To improve the acidity of the bare Kaolin clay, adding some elements into its framework is essential. Many researchers have reported that modified Kaolin clay catalysts can catalyze vegetable oils with methanol to produce FAME (Dang et al., 2013). To the best of our knowledge, no scientific papers have been published on the use of Ce/Kaolin clay as catalyst for the production of FAME.

A new integrated apparatus for extraction and transesterification of cottonseed oil was developed to produce FAME (Figure 1 and 2). The experiment was performed in a tower reactor equipped with a water-cooled condenser. A certain amount of cottonseed kernel powder was loaded in the accumulator tank at the top of the tower, and the catalysts supported on theta (θ) packing rings (ϕ 3×3) were loaded in the tower body. The catalyst amounts were varied by changing the tower section numbers. Then, desired amount of methanol was pumped to the top of the tower and the cottonseed oil was successfully extracted from the cottonseed kernel powder. It should be noted that the separation and purification process was not conducted after the extraction process. The excess extraction solvent and cottonseed oil flowed into the transesterification reactor. In that case, the methanol acted as reactant in the transesterification reaction. Finally, the FAME can be collected from the outlet of the reaction device. The extraction and transesterification of cottonseed oil were both performed in this integrated apparatus, which can simplify the process and decrease costs significantly.

This paper represents an extension of our previous research and provides a new synthetic route of cottonseed-based FAME (Qian et al., 2010; Cao et al., 2014; Zhu et al., 2014; Gui et al., 2016; Gui et al., 2016). In this study, we introduced cerium on the Kaolin clay to improve the catalyst acidity, and studied its catalytic performance for the transesterification of cottonseed oil to FAME in a new integrated apparatus. The catalysts were characterized by XRD, BET and NH_3 -TPD measurements. The effects of cerium loading, catalyst calcination temperature, methanol flow rate, reaction temperature, reaction time, and catalyst amount were also examined.

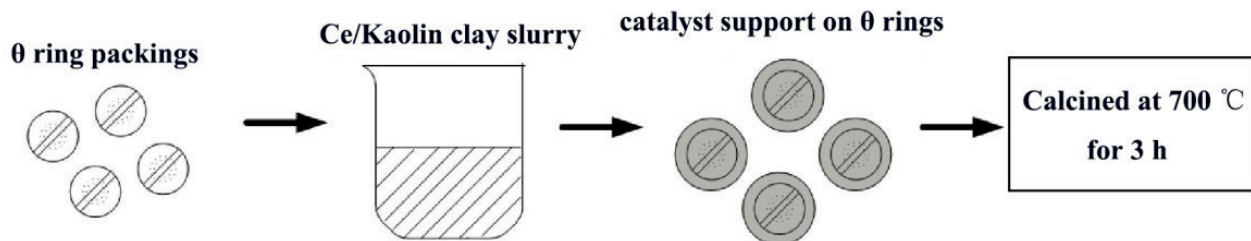


Figure 1. Preparation of the catalyst supported on θ packing rings.

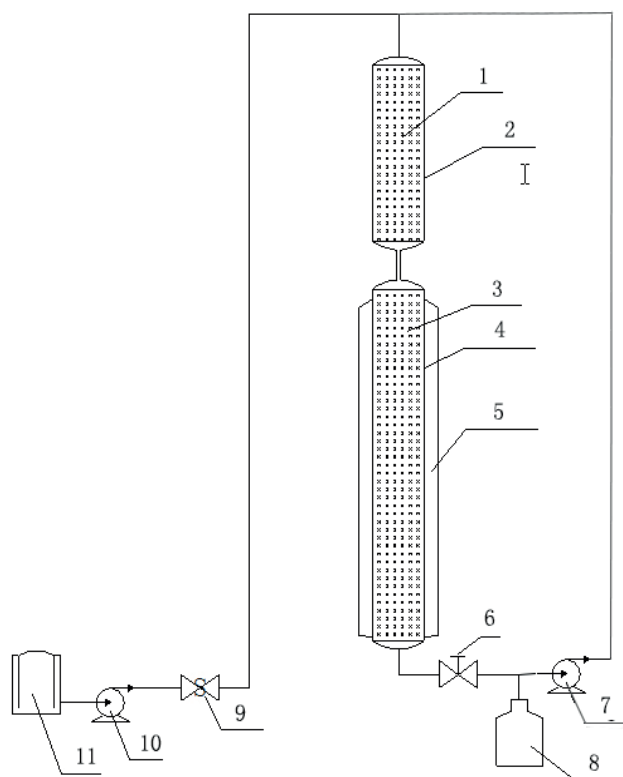


Figure 2. Scheme of the integrated apparatus for FAME production. 1-cottonseed kernel powder; 2-accumulator tank; 3-random packing; 4-column reactor; 5-water bath; 6,9-check valve; 7,10-plunger pump; 8-FAME tank; 11-methanol tank

MATERIALS AND METHODS

Materials

Cottonseeds were obtained from Huaian (Jiangsu, China). Methanol (Aladdin, 99.9%), Kaolin clay, $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (Aladdin, 99%), and H_2SO_4 (Aladdin, 37%) were purchased from Nanjing Wanqing Chemical Co., Ltd. (Nanjing, China). All of the chemicals used in this work were of analytical reagent grade.

Methods

The industrial grade cottonseeds were dried at 110 °C for 24 h, then milled into a fine powder using an electric grinder and sifted through a 60-mesh screen sieve.

According to the ISO 659-1988 and GB/T 14489.1-2008/ISO 665:2000 standards, the oil, moisture and free gossypol contents of the milled cottonseed were 35.4 g/g (wet basis), 6.9 g/g and 0.309 g/g, respectively.

The Ce/Kaolin clay catalysts were prepared by a conventional wet impregnation method (Alves et al., 2014). First, 10 g of Kaolin clay was added into 20 mL of distilled water under stirring. Afterwards, sulfuric acid was added dropwise until the pH reached 3 with constant magnetic stirring at room temperature. Meanwhile, a certain amount of $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ was dissolved in the resultant slurry at room temperature for 24 h. Then, the mixture slurry was supported on the packing ring, dried at 110°C for 12 h, and finally calcined in air for 3h. The modified Kaolin clay samples were denoted as xCe/Kaolin clay ($x = 0-10$ mass% (g/100 g) of Ce loading). The as-prepared catalysts were stored in a desiccators before catalytic tests.

First, 200 g of cottonseed kernel powder was loaded in the accumulator tank at the top of the tower. Next 15 g of catalysts (including the theta packing rings) were preheated in a mixing column with random packing in the tower body. The reaction temperature was controlled at 60 °C by a water bath. Then, 200 mL of methanol was pumped into the top of the tower from the methanol tank and the cottonseed oil was successfully extracted from the cottonseed kernel powder. Afterwards, the excess extraction solvent and cottonseed oil flowed into the transesterification reactor. In that case, the methanol acted as reactant in the transesterification reaction. When the methanol was exhausted, the check valve 7 was opened, then the unreacted methanol and cottonseed oil was continually pumped into the reaction system for circular reaction. Therefore, both the utilization of methanol and the conversion of cottonseed oil were increased. Finally, the FAME can be collected from the outlet of the reaction device.

The procedure was conducted under different reaction conditions: reaction time (1-10 h), reaction temperature (40-80°C), methanol flow rate (2-5 mL/min), and catalyst amount (5-20 g). The obtained reaction mixture was kept in the separating funnel for 12h to separate the glycerol. After that, the excess methanol was removed from the reaction products using a rotary evaporator. To ensure the complete removal of the methanol, the evaporation process was conducted until the weight of samples remained unchanged (Kuk et al., 2005). The products were analyzed by gas chromatography (GC) following the previous literature (Molina Mayo et al., 2015).

Catalyst Characterization

The powder X-ray diffractions (XRD) were conducted on a Shimadzu XRD-6000 powder diffractometer with Cu $K\alpha$ -ray radiation ($\lambda = 0.154$ nm)(40 kV, 40 mA). The diffraction patterns of the samples were recorded from $2\theta = 10-90^\circ$ at a scanning speed of 20°/min.

Temperature programmed desorption of ammonia (NH_3 -TPD) was used to test the acidity of the samples. 0.1 g catalyst was pretreated in He (40 mL/min) at 500 °C for 1h, and the sample was treated with ammonia after cooling down to 100 °C. Then, the catalyst was purged with He. Finally, NH_3 -TPD experiments were conducted in He from 100 to 700 °C at a heating rate of 20°C/min, then the NH_3 -TPD data could be collected.

Brunauer-Emmett-Teller (BET) surface area analysis was conducted to characterize the specific surface area and pore size distribution of the samples. Analysis was conducted using a Quantachrome Autosorb-1 with nitrogen adsorption-desorption at -196°C . The degasification was performed under vacuum at 200 °C for 2 h before the adsorption measurements.

The reaction products were analyzed using a GC-6890 gas chromatograph equipped with a flame ionization detector (FID) and AT.SE-30 capillary column (50 m \times 0.53 mm \times 3 μm). Methyl salicylate was used as an internal standard and n-hexane as solvent. 1 mL of product was dissolved in 0.2 mL of methyl salicylate and 8 mL of n-hexane with vigorous stirring. 1 μL of the mixture was injected into the GC. The column temperature was 180 °C, the temperature of injector and detector were 260 °C. The flow rates of hydrogen, nitrogen, and air were 40, 19, and 300 mL/min, respectively.

In the chromatographic operation conditions, a typical chromatogram is shown in Figure 3. According to Figure 3, the order of peaks corresponds to the solvent n-hexane, methyl salicylate, methyl palmitate, methyl oleate, and linoleic acid methyl ester, respectively.

The yield of FAME was calculated as follows:

$$B(\%) = \frac{S_2 \times f' \times m_2}{S_1 \times m_1} \times 100$$

where: m_1 is the mass of FAME, m_2 is the mass of internal standard added to the sample, S_1 is the peak area of internal standard, S_2 is the peak area of FAME, f' is the correction factor.

RESULTS AND DISCUSSION

Catalyst Characterization

The XRD patterns of the Ce/Kaolin clay catalysts calcined at 700 °C with different Ce loadings are shown in Figure 4. It is obvious that all samples show a very strong peak at about $2\theta=26.08^\circ$, which is commonly attributed to the formation of amorphous phase of SiO_2 . Moreover, three weak peaks are also observed at $2\theta=16.34^\circ$, 35.20° and 40.82° . These peaks confirm the triclinic structure which is the typical characteristic of Kaolin clay materials. In addition, the peak at $2\theta = 28.52^\circ$ is obviously observed on the Ce/Kaolin clay catalysts, which corresponds to

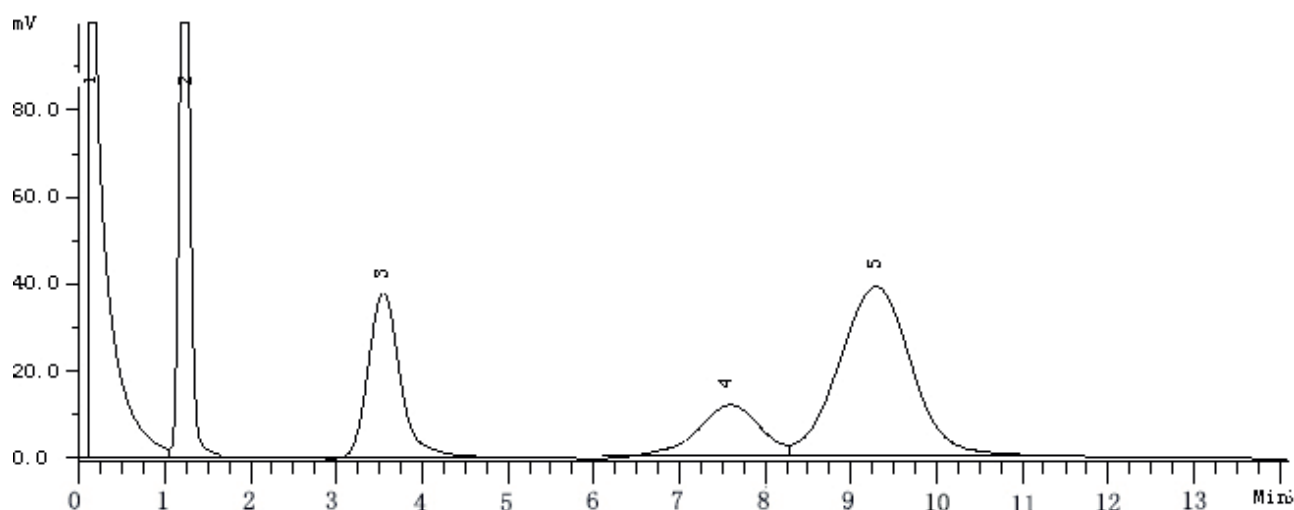


Figure 3. Chromatogram of the product.

the indexed CeO_2 cubic system, unit cell and cubic face centered space group (Nascimento et al., 2015; Nascimento et al., 2014). The results indicate that Ce is successfully incorporated into the Kaolin clay support. It is worth noting that the intensity of the peak increases gradually when the cerium loading increases from 0.025 to 0.1 g/g, which is due to a large amount of Ce on the support. Moreover, when the cerium loading is up to 0.1 g/g, a strong peak is observed at $2\theta=47.48^\circ$, suggesting that part of the cerium crystal structure is changed.

The physical properties of the catalysts play an important role during the transesterification reaction (Dang et al., 2013). The specific surface area, pore volume and pore size of the samples were examined, and the results are shown in Table 1. The surface area of the raw Kaolin clay is $8.91 \text{ m}^2/\text{g}$, and the surface areas of the 2.5Ce-Kaolin clay, 5Ce-Kaolin clay, 7.5Ce-Kaolin

clay and 10Ce-Kaolin clay are $8.70 \text{ m}^2/\text{g}$, $8.13 \text{ m}^2/\text{g}$, $7.27 \text{ m}^2/\text{g}$, and $5.38 \text{ m}^2/\text{g}$, respectively. It is observed that the surface area of the catalysts decreases with increasing cerium loadings, which is due to the fact that the cerium is deposited on the Kaolin clay support. Furthermore, it can be seen that the pore volume decreases and the pore diameter increases with increasing cerium loadings. In fact, the size of triglycerides is estimated at around 3-5 nm, which is much smaller than that of the modified Kaolin clay catalysts (López Granados et al., 2007). Therefore, the diffusion restriction of triglyceride molecules into pores and cages of the modified Kaolin clay catalysts can be avoided. Certainly, larger pore size is beneficial for reactant/product molecules to diffuse to the active sites, thus improving the catalytic activity of the catalysts (Wong et al., 2015).

The NH_3 -TPD profiles of the modified Kaolin clay catalysts are shown in Figure 5. It is obvious that the catalysts exhibit a weak peak from 150°C to about 350°C and a strong peak from 550°C to about 700°C , suggesting that the catalysts have weak and strong acid sites. With the increase of the cerium loading from 0 to 0.05 g/g, the intensities of the corresponding peaks increase, indicating that the acidity of the catalysts increases gradually. The increased acidity is due to dispersed cerium on Kaolin clay and the acidity can be adjusted by loading different amounts of cerium. In addition, the result also shows that the maximum acidity is achieved when the cerium loading is 0.05 g/g. However, the acidity of the catalysts decreases when the cerium loading is over 0.05 g/g, which is due to active sites of the catalysts being covered with excess cerium. It is noteworthy that the acidity of the catalysts has a great impact on the catalytic activity during the transesterification reaction.

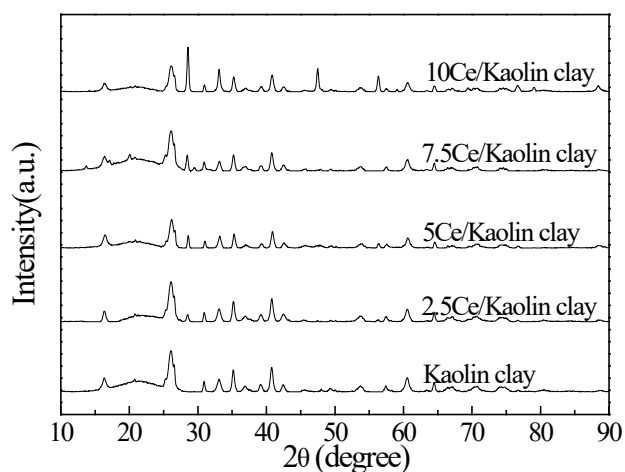


Figure 4. X-ray diffraction patterns of Ce/Kaolin clay with different Ce loadings.

Table 1. Surface Characteristics of Raw and Modified Kaolin Clay Catalysts.

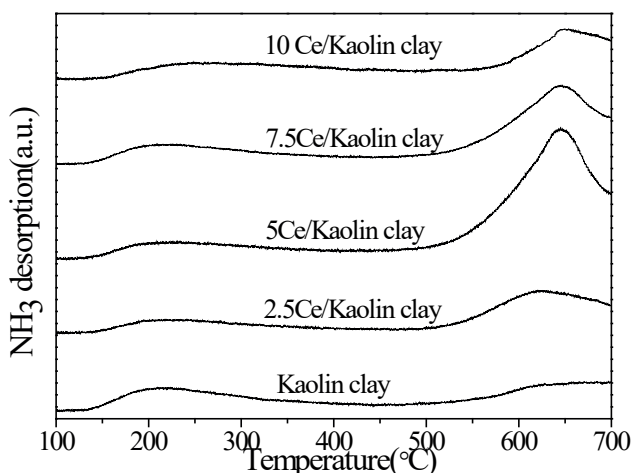
Catalyst	Surfacearea (m ² /g)	Porevolume (cm ³ /g)	Poresize(nm)
Kaolin clay	8.91	0.043	19.24
2.5Ce/Kaolin clay	8.70	0.040	19.82
5Ce/Kaolin clay	8.13	0.033	21.53
7.5Ce/Kaolin clay	7.27	0.025	26.94
10Ce/Kaolin clay	5.38	0.018	35.66

Effect of Cerium Loading on FAME Yield

The FAME yields over the modified Kaolin clay catalysts were investigated by adjusting the cerium loading. The cerium loading ranging from 0 to 0.1 g/g has a significant effect on the catalytic activity. The catalytic results are shown in Figure 4. It can be seen that bare Kaolin clay catalyst show low FAME yield (35%). This is likely due to the fact that bare Kaolin clay show low acidity which can be seen in Figure 6; thus, the transesterification reaction cannot be achieved. Surprisingly, it is obvious that the modified Kaolin clay catalysts are more active. As the cerium loading increases, the acidity of the catalyst enhances, thus the FAME yield is increased significantly. In addition, the results also show that the maximum FAME yield (88%) is obtained with 0.05g/g cerium loading, since the 5Ce/Kaolin clay has more acidity compared to the other catalysts. However, when the cerium loading increased further, the FAME yield dropped rapidly. This might be because the specific surface area, pore volume and acidity of the catalysts decrease when the cerium loading is over 0.05 g/g. Thus, the cerium loading was fixed at 0.05 g/g.

Effect of Catalyst Calcination Temperature on FAME Yield

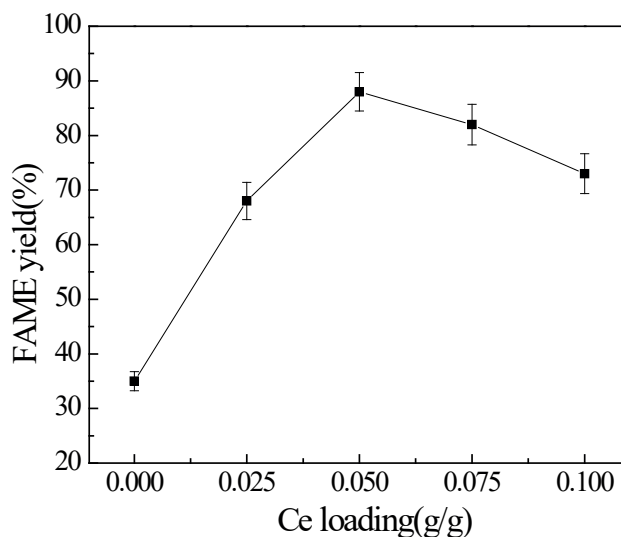
The influence of the calcination temperature ranging from 500 °C to 900 °C for the transesterification of cottonseed oil over 5Ce/Kaolin clay was investigated,

**Figure 5.** NH₃-TPD spectra of raw and modified Kaolin clay catalysts.

as shown in Figure 7. It is obvious that the catalytic activity of the 5Ce/Kaolin clay is related to the catalyst calcination temperature. When the catalyst calcination temperature increases from 500 to 700 °C, the FAME yield shows a rapid increase from 60 to 90%. However, the yield of FAME decreases upon increasing the calcination temperature further, which may indicate that the Ce/Kaolin clay catalyst tends to decompose when calcined at high temperature. Therefore, 700 °C is the most suitable calcination temperature for Ce/Kaolin clay for the transesterification reaction.

Effect of Dosage of Methanol on Cottonseed Oil Extraction

It is well known that commercial methanol is an efficient solvent for extracting oil from oilseeds. The dosage of methanol used is an important parameter during the extraction of cottonseed oil. The dosage of the methanol is controlled by adjusting the flow rate of methanol. The flow rate of methanol from 2.0 to 5.0 mL/min was studied, and the results are shown in Figure 8. The extraction rate of cottonseed oil increases with the increase of the dosage of methanol from 2.0 to 4.0 mL/min, and the extraction time

**Figure 6.** Influence of cerium loading on FAME yield. Reaction conditions: 200 g of cottonseed kernel powder, 15 g of catalyst, 5 mL/min methanol phase rate, and reaction temperature=50°C.

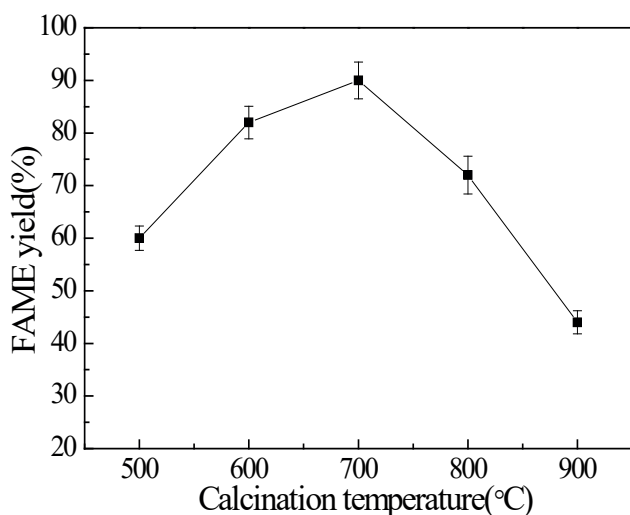


Figure 7. Influence of catalyst calcination temperature on FAME yield. Reaction conditions: 200 g of cottonseed kernel powder, 15 g of catalyst, 5 mL/min methanol phase rate, and reaction temperature = 50 °C.

reduces with the increasing dosage of methanol. When the flow rate of methanol reaches 4.0 mL/min, the extraction rate of cottonseed oil is 96.3% after 3 h of extraction. It is evident from Figure 8 that the excess methanol added to the reaction has a slight effect on the yield of cottonseed oil. Thus, the optimum methanol flow rate is 4.0 mL/min and the extraction time is 3 h.

Effect of Dosage of Methanol on FAME Yield

In order to study the optimum methanol dosage for the transesterification reaction, the effect of different molar ratio of the alcohol to oil by adjusting the flow rate of methanol from 2.0 to 5.0 mL/min over 5Ce/Kaolin clay was investigated, as shown in Figure 9. From the results, the FAME yield enhances gradually upon increasing the methanol flow rate from 2.0 to 4.0 mL/min. It can be seen that no obvious increase of FAME yield is observed upon increasing the methanol flow rate to 5.0 mL/min. Therefore, the optimum methanol flow rate is 4.0 mL/min in this transesterification reaction. Moreover, the excess alcohol during the transesterification reaction was recovered by distillation and reused in the next reaction cycle.

Effect of Reaction Temperature on FAME Yield

The reaction temperature is found to have a considerable influence on the yield of FAME (Demirbas, 2009). To investigate the optimum temperature for the transesterification reaction, a series of reactions over 5Ce/Kaolin clay were performed by changing the temperature from 40 to 70 °C (Figure 10). From Figure 10, it is clearly seen that the yield of FAME noticeably increases with the reaction temperature increase from 40 to 70 °C. However,

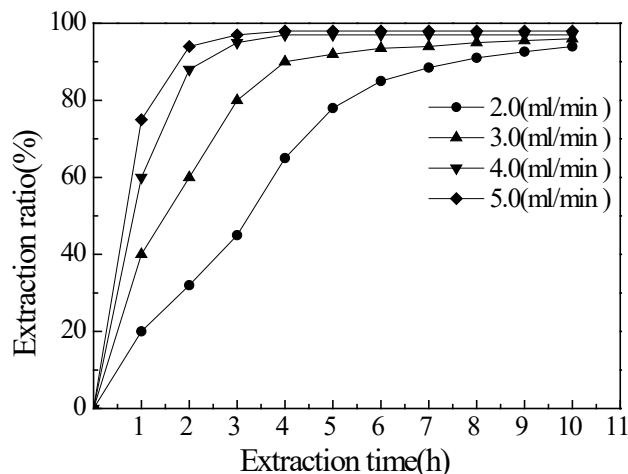


Figure 8. Influence of dosage of methanol on cottonseed oil extraction. Reaction conditions: 200 g of cottonseed kernel powder, ambient temperature, and 10 h of extraction time.

when the reaction temperature reached 70 °C, the reaction temperature is close to the boiling point of methanol, which leads to the vaporization of a large amount of methanol. Furthermore, unexpected and uncontrollable liquid back-up flooding was also observed (Gui et al., 2016). So the optimum reaction temperature for the transesterification reaction is 60 °C.

Effect of Catalyst Amount on FAME Yield

The effect of the amount of 5Ce/Kaolin clay, ranging from 5 to 20 g, on the FAME yield was studied for the transesterification reaction (Figure 11). According to the previous literature, a higher amount of the catalyst is essential to increase the FAME yield (Yee et al., 2011). Figure 9 shows that the yield of FAME increases with increasing catalyst amount from 5 to 15 g, but only a slight increase of the FAME yield is observed with further increase in the catalyst amount. So 15 g of 5Ce/Kaolin clay catalyst was chosen as the optimum catalyst amount for the transesterification reaction.

Reusability of the Catalyst

Reusability is regarded as the fundamental condition for manufacturing as it decreases the production cost of FAME (Alhassan et al., 2015). In order to investigate the reusability of the Ce/Kaolin clay catalyst, the transesterification of cottonseed oil was performed with methanol under optimized reaction conditions. The reusability results are presented in Figure 12. As shown in Figure 10, when Ce/Kaolin clay is recycled 1, 2, 3, and 4 times, the FAME yield is 91%, 86%, 79%, and 74%, respectively. On increasing the number of cycles,

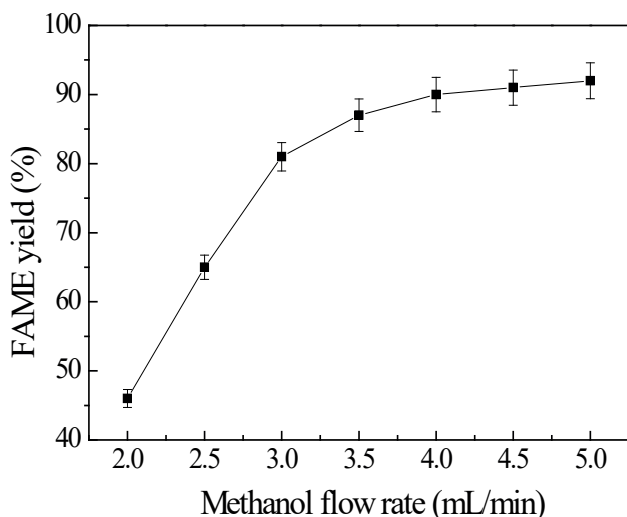


Figure 9. Influence of dosage of methanol on FAME yield. Reaction conditions: 200 g of cottonseed kernel powder, 15 g of catalyst, reaction temperature = 50 °C, and 3 h reaction time.

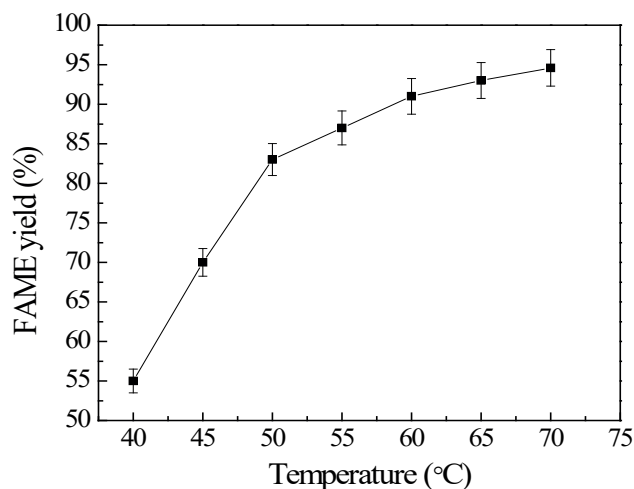


Figure 10. Influence of reaction temperature on FAME yield. Reaction conditions: 200 g of cottonseed kernel powder, 15 g of catalyst, 4.0 mL/min methanol phase rate, and 3 h reaction time.

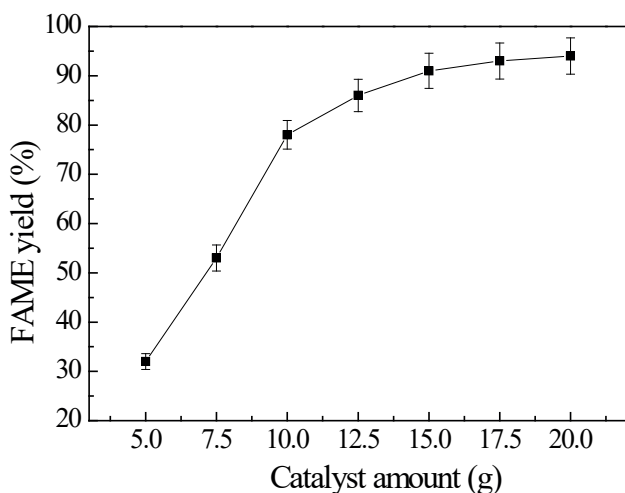


Figure 11. Influence of catalyst mass amount on FAME yield. Reaction conditions: 200 g of cottonseed kernel powder, 15 g of catalyst, 4.0 mL/min methanol phase rate, reaction temperature = 60 °C, and 3 h reaction time.

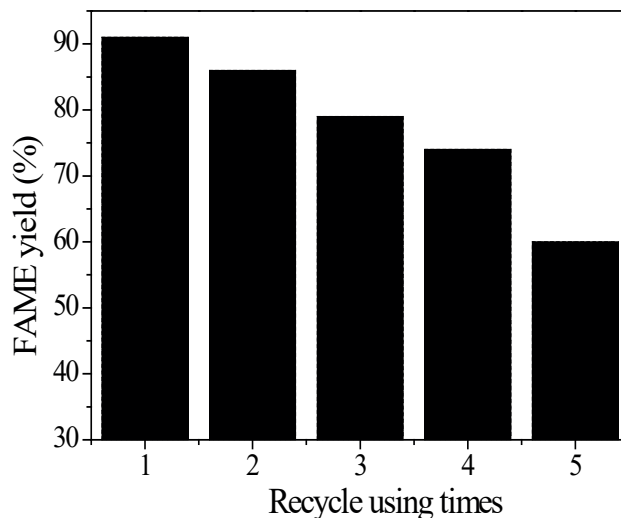


Figure 12. Reusability of the catalysts. Reaction conditions: 200 g of cottonseed kernel powder, 15 g of catalyst, 4.0 mL/min methanol phase rate, reaction temperature = 60 °C, and 3 h reaction time.

part of the catalysts was desquamated from the theta (θ) packing rings and the catalytic performance decreased noticeably. When the catalyst was used for five times, the FAME yield reduced to 60%. The results show that the catalyst can be recycled four times without significant loss of activity.

CONCLUSIONS

An efficient solid acid catalyst (Ce/Kaolin clay) was synthesized and investigated for the extraction and transesterification of cottonseed oil to FAME in a new integrated apparatus. The results showed that the Ce/Kaolin clay catalysts could effectively catalyze

cottonseed oil to produce FAME. The maximum FAME yield (91%) was achieved under the optimal conditions of 700 °C catalyst calcination temperature, 0.05 g/g cerium loading, 4.0 mL/min methanol flow rate, 60 °C reaction temperature, 3 h reaction time, and 15 g catalyst. The results also indicated that Ce/Kaolin clay showed an excellent catalytic stability with the yield of FAME as high as 74% after recycling for 4 times. The highest FAME yield was slightly higher than the reported literature (Silva et al., 2014) which used KF/Clay as catalyst for FAME preparation at a yield of 89.2%. These results showed that the modified Kaolin clay is a promising catalyst for the transesterification of cottonseed oil with methanol to produce FAME.

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