

# Mixed and ground KBr-impregnated calcined snail shell and kaolin as solid base catalysts for biodiesel production



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## ABSTRACT

Mixed and ground activated snail shell and kaolin catalysts impregnated with KBr were investigated. The snail shell and kaolin were calcined, mixed, and ground prior to immersion with KBr solution and subsequent activation at 500 °C for 3 h. The precursor and catalysts were characterized by thermal gravimetric analysis, Fourier transform infrared spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy, scanning electron microscopy, and Brunauer–Emmett–Teller surface area. The catalytic performance of the prepared catalysts was evaluated by transesterification of soybean oil with methanol. The effects of various parameters on biodiesel yield were investigated. A biodiesel yield of 98.5% was achieved using the catalyst prepared by 40% KBr-immersed, mixed, and ground snail shell and kaolin, which were activated at 500 °C. The transesterification conditions were as follows: reaction temperature, 65 °C; reaction time, 2 h; methanol-to-soybean oil molar ratio, 6:1; and catalyst amount (relative to the weight of soybean oil), 2.0 wt%. The solid catalyst could be reused for four times, and biodiesel yield remained over 73.6% for the fourth time.

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## 1. Introduction

The declining fossil fuel resources, along with the gradual global climate warming and pollution caused by fossil fuels, has spurred the development of renewable alternative energy sources. Non-toxic, renewable, high-cetane number, biodegradable, high-flash point, and environmentally friendly biodiesel has emerged as a substitute for traditional fossil fuels [1–3]. According to the Association of American Material Experiment (ASTM), biodiesel refers to vegetable oils and animal fats or other renewable biological resources as raw materials through the transesterification production of long carbon chain fatty acid ester [4–6].

Among the biodiesel preparation methods, the transesterification reaction with conventional catalysts surpasses the traditional homogeneous acid and alkali catalyst transesterification [7–11]. This process, which uses traditional acid and base catalysis, is the most commonly used technique for biodiesel production.

This technique is characterized by easy operation, mild conditions, short reaction time, and high yield. However, the development of transesterification reaction is limited by its highly corrosive catalyst, which is also difficult to separate and purify, in addition to other factors such as the generation of large amounts of industrial waste water and environmental pollution. Thus, the exploration of an environmental-friendly catalyst is becoming a research hot spot in recent years. To overcome the aforementioned disadvantages, heterogeneous solid catalysts have long been investigated. Solid alkali catalysts have attracted much attention because of their high biodiesel yield, fast reaction rate, easy separation from products, and high catalytic activity, which indicate their good prospects for development [12,13].

A solid base refers to compounds in a reaction that can provide electron, exhibit chemical adsorption acid, or discolor the acidic indicator of solids. Biodiesel production by solid base catalysts has been reported in recent years. These catalysts include molecular sieve solid base catalysts, such as Na–X [14] and CaO/NaY [15] molecular sieves, anion exchange resin catalyst [16,17], metal oxides, such as CaO·MgO and SrO [18–23], supported solid base catalyst [24–29], and resin-type solid base catalysts [30,31]. Among the solid base catalysts, CaO exhibits active catalytic performance, mild reaction conditions, readily available raw materials, low cost,

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non-corrosiveness, and high recyclability in transesterification reaction. In addition, calcium, such as egg shell, shell, and bone, is naturally abundant. Boro et al. [21] prepared a series of Li doped egg shell derived CaO for biodiesel production from nonedible oil feedstock. Under optimum reaction conditions, biodiesel yield reached 94%. Liu et al. [22] through numerous experiments compared the catalytic activities of  $K_2CO_3/\gamma-Al_2O_3$ ,  $KF/\gamma-Al_2O_3$  with CaO. Results show that CaO had better reusability and maintained high activity even after 20 uses. Additionally, the activity of  $K_2CO_3/\gamma-Al_2O_3$ ,  $KF/\gamma-Al_2O_3$  is reduced after use that significantly affected biodiesel yield. The right amount of water content also significant affected the biodiesel yield in this experiment, because it increased the basic characteristics of the CaO active site. Boey et al. [32,33] calcined crab shells as biodiesel transesterification catalyst and performed a statistical analysis using central composite design. Analytical results show that catalyst concentration, reaction temperature, catalyst amount, catalyst concentration, and methanol-to-oil molar ratio are the most important factors affecting biodiesel purity. Moreover, the catalyst reusability test showed that the catalyst could be used 11 times without losing its activity. Viriya-empikul et al. [34] calcined mollusk shells of snail at 800 °C for 2 h–4 h. CaO was formed at temperatures above 800 °C, with the product of calcination as catalyst for biodiesel transesterification reaction, and the conversion rate reached over 90% after 2 h. Experimental results show that the surface area of the catalyst affected the catalyst performance. Boro et al. reported the use of Mumbai local shell shad as catalyst under the following conditions: calcinations temperature, 800 °C; catalyst amount, 3 wt %; methanol/oil ratio, 9:1; and activation temperature, 65 °C ± 5 °C. They obtained 93.3% yield. Rezaei et al. [35] used discarded mussel shells as a catalyst by calcinations at different temperatures. Instrumental analytical results showed that the catalyst had high catalytic activity at 1050 °C. Under optimal reaction conditions, the biodiesel purity and yield were 100% and 94.1%, respectively. The results showed that the activity of the recycled catalyst was deactivated because of the reduced amount of Ca on the surface. Given the instability and poor recycling rate of the produced catalyst, a low-cost, environment-friendly, high-catalytic performance, and reusable solid base catalyst should be established.

Kaolin, another natural substance [36], is good catalyst for biodiesel production, but it does not exhibit high catalytic activity when used alone. To enhance the high-catalytic performance of CaO and kaolin catalyst, experiments have been performed to prepare a highly efficient, inexpensive, green, environmentally friendly solid base catalyst. The present study mixed and ground different proportions of kaolin and snail shells after high-temperature calcination. Then, the catalyst was immersed with different K<sup>+</sup> concentrations solution, because K<sup>+</sup> show good catalytic performance. Numerous studies have reported on the load of K<sup>+</sup> such as MgO [37], CaO [38], ZrO [39], SiO<sub>2</sub> [40], shell [41], and so on. Qiu F. et al. used a solid base nanocatalyst prepared by ZrO<sub>2</sub> loaded with C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>HK and achieve the biodiesel yield of 98.03% [39]. Jairam S. et al. Used KI-impregnated calcined oyster shell as a solid catalyst for transesterification of soybean oil and achieved a maximum conversion of 95% [41]. But none of them achieved a maximum conversion of 98%. KBr solution was used in this study because of its better solubility. The ground mixture was soaked in KBr to load K<sup>+</sup> and then calcined to obtain high activation. The resulting catalyst showed good morphology and high dispersion of the active component for efficient biodiesel preparation under mild conditions. This high-performance catalyst did not produce saponification and emulsification during the catalytic reaction. The prepared catalysts were characterized by thermal gravimetric analysis (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier-transform infrared (FTIR) spectroscopy, X-ray photoelectron

spectroscopy (XPS), and Brunauer–Emmett–Teller (BET) methods. The effects of catalyst preparation conditions and various reaction variables on the biodiesel yield were also investigated. The stability and reusability of the prepared catalyst were also determined.

## 2. Experimental

### 2.1. Material

Commercial edible-grade soybean oil was purchased from the local supermarket. (Shanghai, China) and used without further purification. Snail shells were collected from the local seafood market. Kaolin, n-hexane, KBr, and anhydrous methanol were of analytical reagent grade and purchased from Sinopharm Chemical Reagent Co. Ltd., (Shanghai, China). Methyl laurate (internal standard) was of chromatographic grade and purchased from Sinopharm Chemical Reagent Co. Ltd. Anhydrous methanol were AR grade and purchased from Sinopharm Chemical Reagent Co. Ltd., (Shanghai, China) ( $H_2O \leq 0.05\%$ ).

### 2.2. Catalyst preparation

First, the residue inside the collected snail shell was removed, and the shell was washed with hot water and placed in an oven at 100 °C for 12 h. The snail shells were then dried and calcined in a muffle furnace at 700 °C–900 °C for 3.5 h. The kaolin was calcined in a muffle furnace at 800 °C for 10 h to remove hydroxyl. Then, the calcined kaolin and snail shell were ground at different ratios using a mortar. The ground catalyst were added to different concentrations of KBr solution for 3 h–6 h with warm water, then filtrated and placed in a drying oven at 110 °C for 12 h. Finally, the dried catalyst was calcined in a muffle furnace for 3 h at 450 °C–650 °C to activate the catalyst performance. The prepared catalysts were ground and stored in desiccator until further use.

### 2.3. Catalyst characterization

TGA, XRD, SEM, FTIR, XPS, and BET were applied to evaluate the change in the structure and morphology of the fresh and used catalysts. The weight loss behavior of KBr supported on ground kaolin and snail shell during activation was measured using a thermobalance (TA Q5000IR). Samples were heated to 800 °C at a heating rate of 10 °C/min under N<sub>2</sub> flow. The XRD pattern of the catalyst was studied on an X-ray diffractometer (X, Pert PW 3040/60) at 2θ angle, with scan range of 10°–80°. The XRD patterns of the catalyst were obtained with Cu Kα radiation ( $k = 0.15406$  nm) at 40 kV, 30 mA, scan speed of 4.0°/min, and scan range of 10°–80°. Functional groups attached to the catalyst surface were determined by FTIR (Nicolet 6700), which used the KBr pellet technique which recorded in the 4000  $cm^{-1}$ –400  $cm^{-1}$  range with a resolution of 4  $cm^{-1}$ . Furthermore, the morphology was observed on a ultra-resolution field-emission scanning electron microscope (Model S-3400N Hitachi). The chemical composition of the major elements present in the catalysts material were analyzed by XPS (Model ESCALAB 250, Thermo-VG Scientific). The specific surface area, mean pore diameter, and pore volume were determined the BET method (model: ASAP2020M+C).

### 2.4. Transesterification reaction and method of analysis

The transesterification reaction of soybean oil with methanol was performed in a 500 mL three-neck round-bottomed flask equipped with a mechanical stirring bar, a thermometer, and reflux condenser. The typical reaction procedure was as follows. First, 50 mL (45.6 g) of soybean oil, 13 mL anhydrous methanol

(methanol/oil molar ratio of 6:1, based on a previous study [19]), and 0.92 g catalyst (2 wt% mass of the oil) were placed into the flask. Then, the mixture was heated, and the temperature was maintained at 65 °C for 2 h. The reaction was quickly stopped by cooling in icy water after reaching a predetermined reaction duration. When the transesterification reaction was finished, the solid base catalyst was removed from the reaction mixture via centrifugation at 4000 rpm for 20 min. Glycerol was then separated using a separating funnel, and the excess methanol and trace water were separated from the liquid phase via rotary evaporation at 80 °C for 1 h. The fatty acid methyl esters (FAME) was analyzed following the EN14103 method. A gas chromatograph–mass spectrometer (GC–MS–QP2010Ultra) was used to identify the components of the biodiesel on the basis of the MS data to the NIST library and the retention time between the samples and standard compounds. The biodiesel yield was determined by a gas chromatograph (Shimadzu GC–2014) equipped with a flame ionization detection system and a capillary column (Rtx-65 30 m × 0.32 mm × 0.25 μm). Methyl laurate was used as an internal standard and n-hexane as solvent. The biodiesel samples and internal standard were weighed accurately and diluted with n-hexane. Then, 1 μL of diluted sample was injected into the GC to determine biodiesel yield. The inlet temperature of the sample into the injector was 50 °C, which was heated up to 270 °C at a rate of 30 °C/min and maintained at 270 °C for 10 min. The temperatures of both the injector and detector were maintained at 285 °C, and nitrogen was used as the carrier gas. The split ratio was 20:1. The biodiesel yield was calculated based on the literature [42] using Eq. (1).

$$\text{Biodiesel yield} = (m_1 \times A_2) / (m_2 \times A_1) \times 100\% \quad (1)$$

$m_1$  and  $m_2$  are the weights of the internal standard and biodiesel, respectively.  $A_2$  and  $A_1$  are the areas of the total FAME obtained from soybean oil and internal standard, respectively. The experiments were performed twice, and data shown are the average values within ±2.0% errors.

### 2.5. Catalyst stability and reutilization

The recyclability of the catalyst was tested. The solid catalyst was recovered by centrifugation after first run reaction under the optimal reaction conditions. Prior to any reuse, the waste catalyst was washed by methanol. A mixture of methanol and the catalyst was heated at 90 °C on a low speed mixer until the methanol was evaporated. Then, the used catalyst was activated at 500 °C to remove the adsorbed glycerol and used in the next run of transesterification between soybean oil and methanol under the same reaction condition. Several experiments were performed to test the repeatability of the catalyst.

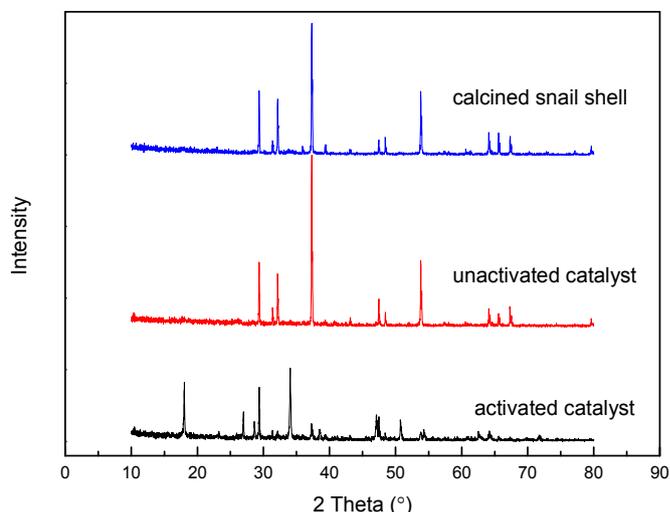
### 2.6. Biodiesel properties

The acceptability of the biodiesel product was determined by testing the product according to the test methods recommended by ASTM and EU methods as follows: density (EN ISO 3675), kinematic viscosity (ASTM D 445), flash point (ASTM D 93), water content (ASTM D 1796), copper strip corrosion (ASTM D 130), sulfur content (ASTM D 2622), free and total glycerol (ASTM D 6584), cold filter plugging point (EN 590), and cloud points (EN 590).

## 3. Results and discussion

### 3.1. Catalyst characterization

The XRD patterns of the calcined snail shell, as well as the

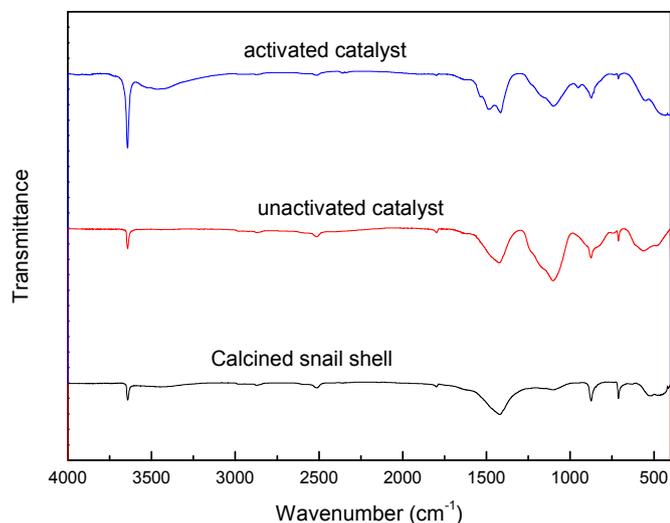


**Fig. 1.** The XRD pattern of calcined snail shell, unactivated catalyst (calcined snail shell/kaolin Mixing and grinding) and activated catalyst (impregnation with KBr and activation at 500 °C).

unimpregnated and impregnated activated mixed and ground snail/kaolin, are shown in Fig. 1. Comparative results of the XRD patterns of the different catalysts show slight difference in the curve of the three substance catalysts, that is, between the calcined snail shell and the ground and mixed calcined snail shell/kaolin. All substances have peak at  $2\theta = 28^\circ\text{--}35^\circ$ . A strong peak is found near  $37^\circ$ , and another peak at  $54^\circ$ . Small difference appeared at around  $2\theta = 33^\circ$  and  $47^\circ$ . The slight difference may have been caused by the structural change in the calcined snail shell mixed with kaolin. However, when the mixture catalyst was impregnated with KBr and activated in a muffle furnace, the peaks changed more remarkably. Peaks emerged at  $2\theta = 8^\circ, 27^\circ, 29^\circ, 34^\circ,$  and  $48^\circ$ , whereas the peaks at around  $2\theta = 32^\circ, 37^\circ,$  and  $54^\circ$  disappeared. It means the randomness of the molecular structure increased, and the crystallinity of the molecular structure decreased. Meanwhile, more diffraction peaks are found in the XRD results of the tri-step procedure catalyst. This result showed that the crystal structure of the catalyst had a clear change after KBr impregnation. The structural change in the crystal indicates that new chemical bonds could have possibly formed.

The FTIR analytical results for the calcined snail shell, as well as those of the unimpregnated and impregnated activated mixed and ground snail/kaolin, are shown in Fig. 2. Peaks of the calcined snail shell are found at 3642.19 (vibrations of –OH stretching of water), 1421.42 (carbonate group), 874.89, and  $522.18\text{ cm}^{-1}$ . A new absorption peak at  $1103.43\text{ cm}^{-1}$  (asymmetric Al–O vibrations) was formed when the calcined snail was mixed and ground with kaolin. However, significant differences appeared when the mixture was impregnated with KBr and activated. The peak at  $3643.74\text{ cm}^{-1}$  became stronger, and two new peaks at  $1486.49$  and  $952.26\text{ cm}^{-1}$  appeared. New chemical bonds are deduced to be formed in the mixed and ground calcined snail/kaolin after KBr impregnation and activation, and the formation of new chemical bonds have direct relation with KBr impregnation in the mixed catalyst. This result is also confirmed by the XRD results.

SEM was used to analyze the change in the microstructure of the activated catalyst to describe the variation in the catalyst surface area and total pore volume. The catalyst, that was calcined at 800 °C, impregnated with KBr, and activated has favorable surface area and total pore volume features because some small organic molecules were released from the shell to form a porous material

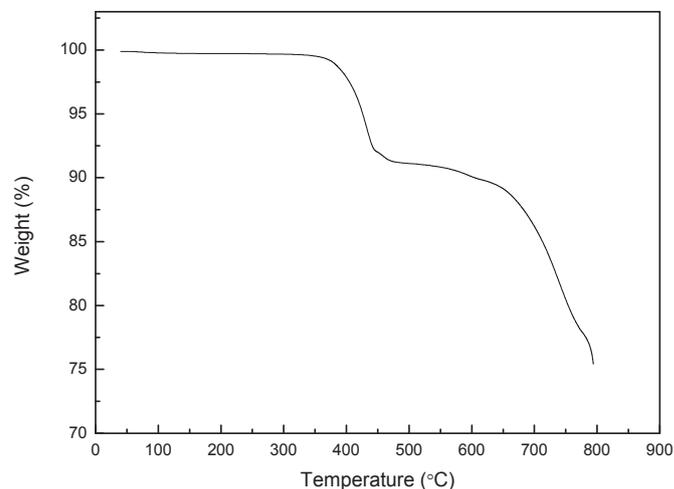


**Fig. 2.** The FT-IR pattern of calcined snail shell, unactivated catalyst (calcined snail shell/kaolin Mixing and grinding) and activated catalyst (impregnation with KBr and activation at 500 °C).

under the aforementioned conditions (Fig. 3a–c). Catalytic activity was enhanced with increasing specific surface area of mixed and ground snail/kaolin. Large specific surface area contributes to catalytic reactions.

The thermal stability of the catalyst was examined by TGA. The TGA profiles of the impregnated and activated mixed and ground snail shell and kaolin are demonstrated in Fig. 4. The DTA curve for the new catalyst exhibits an endothermic peak at 350 °C, which indicates that some new ingredients might have been generated by KBr solution impregnation and mixing and grinding. When the temperature was increased to 350 °C–440 °C, new substance decomposition occurred. The weight loss of all the samples at 600 °C–800 °C could be attributed to the decomposition of snail shell structure. The new catalyst can exist stably below 600 °C without obvious weight loss. However, when activation temperature exceeded 600 °C, a sharp weight loss was observed, and DTA result showed weight loss peaks at 600 °C–800 °C. Thus, the activation temperature should be lower than 600 °C to avoid sharp decomposition of active phase catalyst.

The results of XPS (Table 1) show that for the K<sup>+</sup> content of catalyst surface, when the catalyst was impregnated with KBr and activated under high temperature, numerous K<sup>+</sup> loading could be found on the catalyst surface. The loading K<sup>+</sup> on the catalyst surface resulted in high catalytic activity in the transesterification of



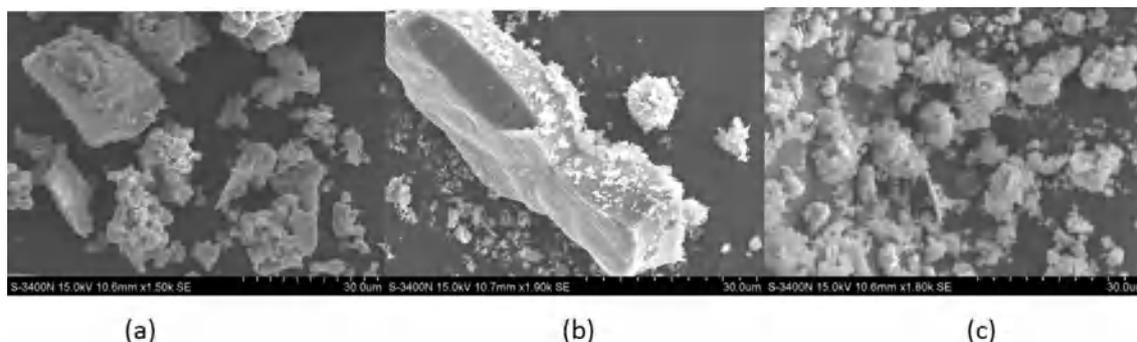
**Fig. 4.** The TGA pattern of activated catalyst (impregnation with KBr and activation at 500 °C).

soybean oil with methanol.

The pore size distribution for the original snail shell and impregnated and activated mixed and ground kaolin are demonstrated in Fig. 5. The original snail shell and the mixed and ground with kaolin sample show a very narrow pore distribution, centered at 2 nm–4 nm pore diameter, which shows a probable mesoporous phase in the catalyst. The pore distribution changed with KBr solution impregnation. The macropores formed by the decomposition of organic substance are associated with the impregnated KBr solution reaction. The macropores of this dimension provided the appropriate space for the generation of active centers and suitable channels for the fast transfer of the product in the reaction.

The N<sub>2</sub> adsorption–desorption curve is demonstrated in Fig. 6. With increase in p/p<sub>0</sub>, the two curves divide, indicating the presence of numerous micropores [Fig. 6(a) and (b)]. When the catalyst was impregnated with KBr solution, the absorbed volume increased. The macropores of this dimension provide appropriate space for the generation of the active centers and suitable channels for the fast transfer of the product in the reaction. This condition is effective in promoting the conversion rate of biodiesel. These data indicated that the structural changes in the calcined snail shell will determine the surface area, total volume, and pore diameter distribution and the catalytic activity.

The BET of the typical catalysts are shown in Table 1. The surface area and pores volume increased when the catalyst was impregnated with KBr solution and activated. This phenomenon may have



**Fig. 3.** The SEM pattern of (a) calcined snail shell, (b) unactivated catalyst (calcined snail shell/kaolin Mixing and grinding) and (c) activated catalyst (impregnation with KBr and activation at 500 °C).

**Table 1**  
Textural parameters of various solid base catalysts and catalytic data on their use in the transesterification of rapeseed oil with methanol.

Sample	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	$V_p$ ( $\text{cm}^3/\text{g}$ )	$\text{K}^+$ content (wt.%)	Biodiesel yield (%)
Calcined snail shell	13.18	0.1493	–	93.2
Unactivated catalyst	5.44	0.0255	–	78.5
Activated catalyst	25.82	0.0469	20.5	98.5

BET<sup>a</sup> means Brunauer–Emmett–Teller.

been due to the fact that when the snail shell was mixed with kaolin, the pores were filled, which led to relatively low surface area. When the catalyst was impregnated with KBr solution and activated at 500 °C, the intercalated KBr decomposed rapidly, and the blocked pores (micropores and mesopores) were opened. Consequently, the surface area of catalyst increased. This result is also consistent with those of the TGA and FTIR.

### 3.2. Effect of catalyst preparation conditions on biodiesel yield

The transesterification of soybean oil with methanol was performed using snail shell and kaolin catalyst under the following conditions: calcination temperature, 800 °C; snail shell-to-kaolin ratio, 4:1; KBr aqueous solution concentration, 40 wt%; and activation temperature, 500 °C. The reaction conditions were set as follows: reaction temperature, 65 °C; reaction time, 2 h; methanol-to-soybean oil molar ratio, 6:1; and catalyst dosage 2% of soybean oil mass.

In this experiment, the biodiesel produced by transesterification of the soybean oil using the new mixture catalyst is transparent, and any subsequent purification step is not necessary. This phenomenon indicates that no saponification occurred during the transesterification of soybean oil with methanol by the new mixture catalyst. Thus, the by-product glycerol can be easily separated from the resultant mixture, and the catalyst can be readily recovered from the reaction mixture. Compared with conventional catalysts biodiesel production from soybean oil, using the new mixture catalyst omitted subsequent costly and chemically wasteful purification steps, indicating that the proposed catalyst is rather ecologically friendly.

#### 3.2.1. Effect of calcination temperature of snail shell

To investigate the effect of calcination temperature on catalytic activity, a series of catalysts were prepared at different calcination temperatures (all samples were treated by 40 wt% KBr solution and 500 °C activation temperature) and were used for transesterification of soybean oil with methanol. The yield of transesterification of soybean oil is remarkably improved with an increase in the calcination temperature from 700 °C to 800 °C, as can be seen in Fig. 7. Then, a latten curve was shown beyond 800 °C, and almost no significant change was found at 900 °C. This result shows that the snail shell at 800 °C was completely converted to CaO, and the increase in temperature did not produce any significant change. The optimum calcined temperature for the snail shell material should be 800 °C, which not only reduced energy consumption, but also achieved high biodiesel yield (98.5%).

#### 3.2.2. Effect of the concentration of the KBr solution

The effects of KBr concentration on catalytic activity are shown in Table 2. The transesterification yield improved from 83% to 98.5% when the concentration of KBr solution increased from 10 wt% to 40 wt%. The increase in the concentration of KBr solution contributed to an increase in the active sites in the snail shell and kaolin ground materials. When KBr concentration was beyond 40 wt%, however, the catalytic activity was reduced with increasing KBr concentration, and the transesterification yield gradually declined

to 87% at 50 wt% KBr solution. This behavior indicates that the active sites in the shell have reached a saturation point at 40wt% KBr concentration. Further increase in KBr concentration beyond 40 wt% showed that excessive  $\text{K}^+$  cannot be well dispersed, leading to the polymerization of the active sites. Thus, the optimum concentration of KBr solution is 40 wt%.

#### 3.2.3. Effect of mass ratio of Snail shell to Kaolin

The effects of the calcined kaolin-to- snail shell ratio on the catalytic activity are shown in Table 2. When the snail shell-to-kaolin ratio decreased from 5:1 to 4:1, the transesterification yield improved from 95.3% to 98.5%. Changing the snail shell-to-kaolin ratio from 4:1 to 1:1 improved the transesterification yield from 98.5% to 43%. This phenomenon probably occurred because the excessive kaolin catalyst dispersed in oil and alcohol mixture to form a slurry state did not effectively serve as a catalyst, thereby preventing transesterification. Therefore, to obtain higher yields, the optimum ratio of calcined kaolin and snail shell was chosen as 4:1 in the subsequent experimental analysis.

#### 3.2.4. Effect of activation temperature

The effects of activation temperature on the catalytic activity were investigated from 300 °C to 600 °C, and all the samples were treated at 800 °C for incomplete calcination and 40 wt% KBr solution. The transesterification yield of soybean oil using kaolin and snail shell ground catalysts prepared at different activation temperatures are shown in Table 2. The rate of transesterification initially increased with the increase in activation temperature, then reached the maximum value of 98.5% at 500 °C, and slightly decreased when the activation temperature was over 500 °C. This behavior is probably due to the fact that the number of active sites formed by the reaction of KBr with the partially calcined and ground kaolin and snail shell will increase with the increase in activation temperature under 500 °C. However, the active sites will be decomposed at temperature above 500 °C. Thus, the optimum activation temperature was 500 °C in this study.

### 3.3. Effects of transesterification process variables

#### 3.3.1. Effect of reaction temperature

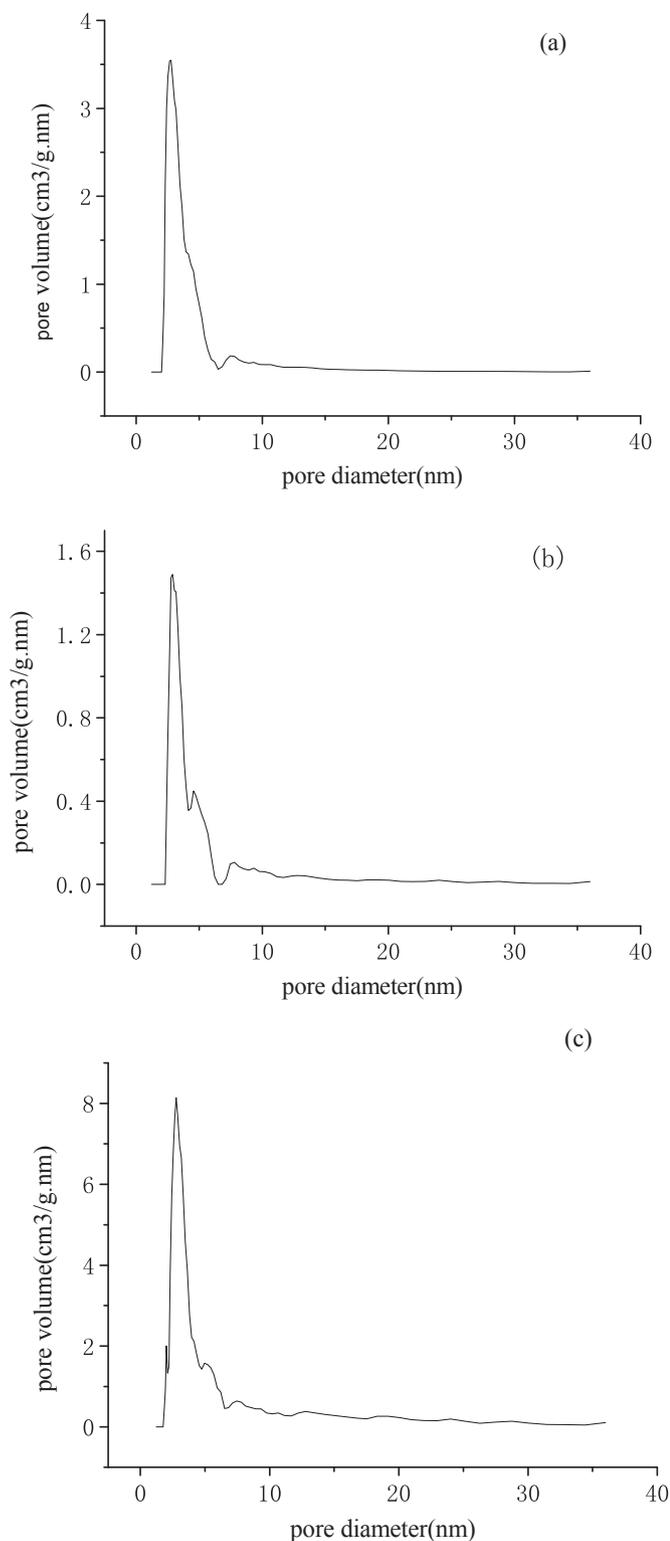
The effect of reaction temperature on the biodiesel yield is shown in Table 2, which also shows the mass percentages of biodiesel at different reaction temperatures. Results indicated that the biodiesel yield increased with an increase in temperature and reached 98.5% at 65 °C. However, the biodiesel yield decreased when the temperature increased to 75 °C. The possible reasons are that when the temperature exceeds the boiling point of methanol, a lot of bubbles of methanol are formed hence inhibiting the mass transfer on the three-phase interface. The effect of evaporative losses of methanol to biodiesel yield was larger than that of the enhanced solubility of methanol in oils. Thus, the optimum reaction temperature of 65 °C was chosen in the subsequent experiments.

#### 3.3.2. Effect of catalyst amount on biodiesel yield

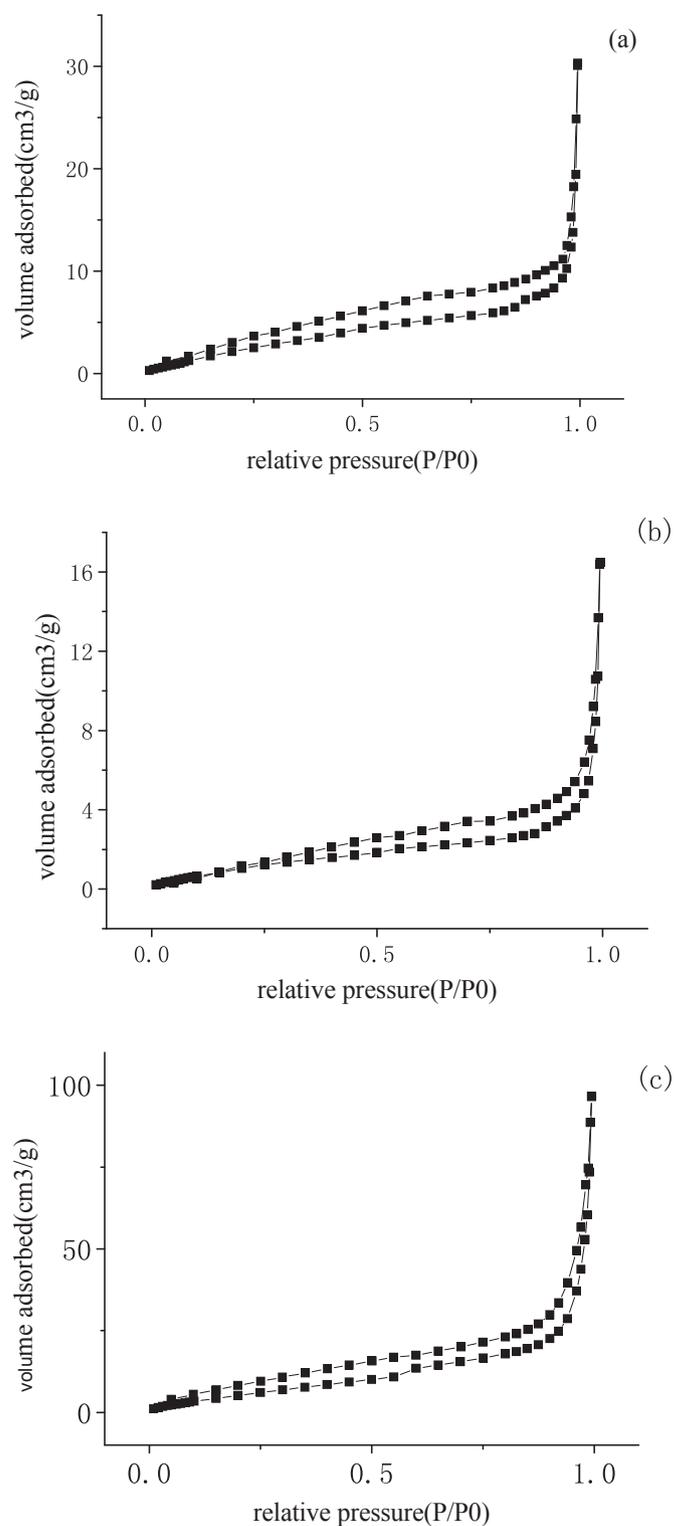
The effect of catalyst amount on biodiesel yield is demonstrated in Table 2. The catalyst concentration was varied from 1 wt% to 5 wt%

% of soybean oil. The biodiesel yield increased from 60.0% to the maximum yield of 98.5% when catalyst amount was increased from 1 wt% to 2 wt%. However, biodiesel yield dropped to 90.4% as the catalyst amount was further increased to 5.0 wt%. The reduced yield is probably because excessive solid catalyst results in too viscous

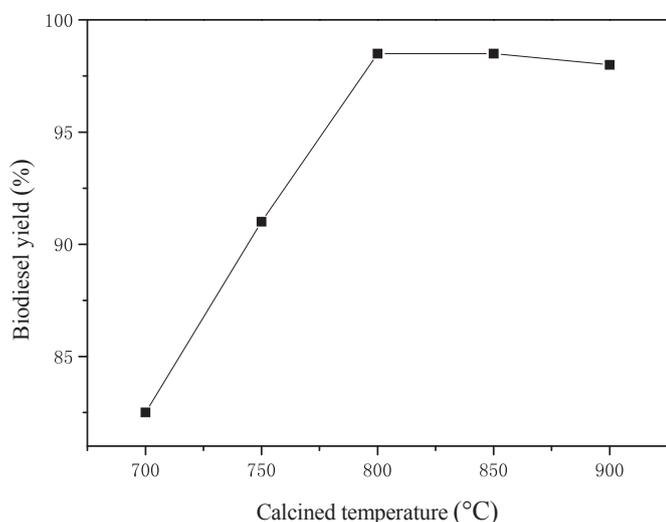
slurry (mixture of solid catalyst and reactants), leading to difficulty in mixing (mass transfer). The high catalyst concentration results in a more viscous reaction mixture, which will increase the mass transfer resistance [43]. However, with low catalyst concentration, the reaction rate to produce FAME was slow. Furthermore, the



**Fig. 5.** The Pore size distribution of catalyst samples (a) calcined snail shell, (b) unactivated catalyst (calcined snail shell/kaolin Mixing and grinding) and (c) activated catalyst (impregnation with KBr and activation at 500 °C).



**Fig. 6.** The N<sub>2</sub> adsorption–desorption curve of catalyst samples (a) calcined snail shell, (b) unactivated catalyst (calcined snail shell/kaolin Mixing and grinding) and (c) activated catalyst (impregnation with KBr and activation at 500 °C).

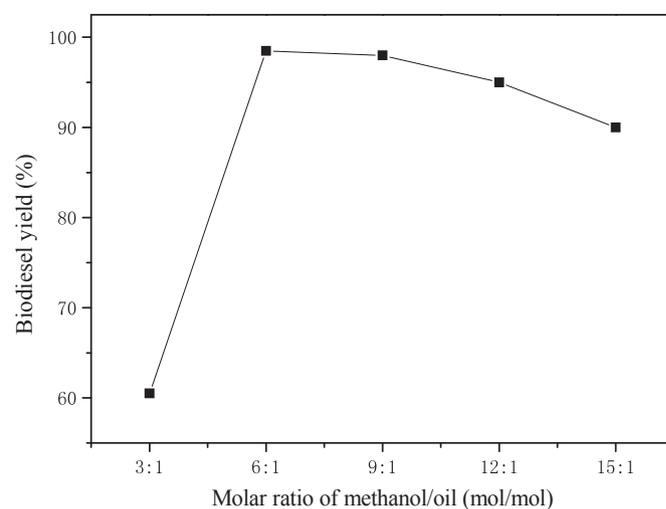


**Fig. 7.** Effect of nail shell calcined temperature on the biodiesel yield. Reaction conditions: oil 50 ml (45.6 g), methanol 13 ml, catalyst 0.92 g and reaction temperature 65 °C, reaction time 2 h.

soybean oil contains a low amount of free fatty acids, so the excessive basic sites in the reaction system can react with the free fatty acids to form soap and water, which reduces the biodiesel yield [35]. The optimum catalyst amount was 2.0 wt%.

### 3.3.3. Effect of reaction time

The effect of reaction time on the methyl ester yield is demonstrated in Table 2. With the increase in reaction time, the biodiesel yield also increased, and the biodiesel has reached the maximum yield of 98.5% after 2 h. No significant change was observed in biodiesel yield when reaction time was increased to 4 h. Thus, 2 h is sufficient in terms of shortening reaction time and reducing energy consumption, the biodiesel can achieve high yields.



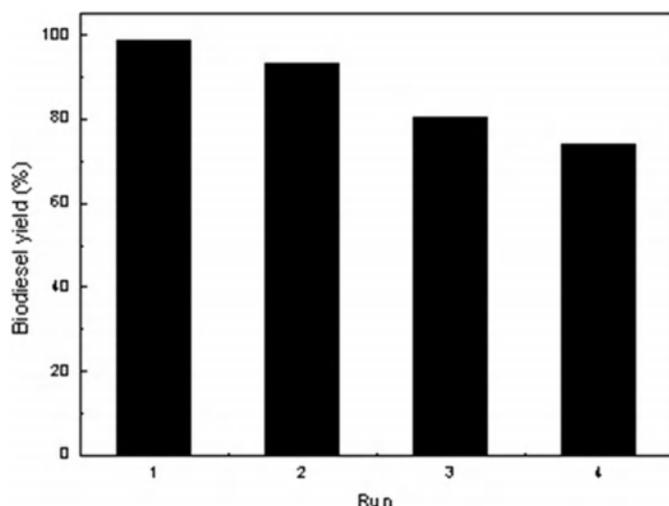
**Fig. 8.** Effect of molar ratio of methanol/oil on the biodiesel yield. Reaction conditions: oil 50 ml (45.6 g), reaction time 2 h, reaction temperature 65 and catalyst 0.92 g.

### 3.3.4. Effect of molar ratio of methanol to soybean oil

One of the most important variables that affect the biodiesel yield was the alcohol-to-soybean oil molar ratio. The stoichiometric ratio for transesterification requires three moles of alcohol and one mole of triglyceride to yield three moles of fatty acid alkyl ester and one mole of glycerol. However, transesterification is an equilibrium reaction, so the ester formation can be increased by employing an excess amount of methanol to drive the equilibrium toward product formation. The effect of methanol-to-oil on the yield is shown in Fig. 8. When the molar ratio increased from 3:1 to 6:1, the biodiesel yield increased from 60.5% to 98.5%. With further increase in methanol-to-oil molar ratio to 15:1, the biodiesel yield decreased. Experimentally, the methanol can dilute soybean oil; that is, a high methanol-to-oil ratio can enable full contact between

**Table 2**  
Optimization of reaction conditions.

KBr concentration (wt%)	Snail shell-to-kaolin ratio	Activation temperature (°C)	Reaction temperature (°C)	Catalyst amount (wt%)	Reaction time (h)	Yield (%)
10	4:1	500	65	2	2	83.0
20	4:1	500	65	2	2	87.0
30	4:1	500	65	2	2	95.5
40	4:1	500	65	2	2	98.5
50	4:1	500	65	2	2	87.0
40	5:1	500	65	2	2	95.3
40	4:1	500	65	2	2	98.5
40	3:1	500	65	2	2	80.0
40	2:1	500	65	2	2	61.5
40	1:1	500	65	2	2	43.0
40	4:1	300	65	2	2	81.0
40	4:1	400	65	2	2	86.5
40	4:1	500	65	2	2	98.5
40	4:1	600	65	2	2	98.0
40	4:1	500	55	2	2	60.0
40	4:1	500	60	2	2	88.0
40	4:1	500	65	2	2	98.5
40	4:1	500	70	2	2	93.0
40	4:1	500	75	2	2	87.0
40	4:1	500	65	1%	2	60.0
40	4:1	500	65	2%	2	98.5
40	4:1	500	65	3%	2	97.0
40	4:1	500	65	4%	2	95.0
40	4:1	500	65	5%	2	90.4
40	4:1	500	65	2	1	60.0
40	4:1	500	65	2	2	98.5
40	4:1	500	65	2	3	98.5
40	4:1	500	65	2	4	98.5



**Fig. 9.** Reuse of the catalyst. Reaction conditions: soybean oil 50 ml (45.6 g), methanol 13 ml, catalyst 0.92 g (first time), reaction temperature 65 °C and reaction time 2 h.

**Table 3**  
Biodiesel component.

Peak#	R. Time	Area%	Mark name
1	23.757	11.75	methyl palmitate
2	31.349	54.06	methyl linoleateter
3	31.515	5.01	methyl linolenate
4	31.702	25.25	methyl oleate
5	33.084	3.93	methyl stearate

reagents and catalyst to accelerate the reaction. However, excessive methanol is not favorable for the transesterification because the catalyst concentration (relative to the total weight of soybean oil and methanol) decreased, and the oil was diluted preventing the access of triglyceride molecules to the active sites. Another possible reason may be the high alcohol content (more than optimal ratio) which interferes with the phase separation of glycerol because of an increase in glycerol solubility in methanol. When glycerol remains in the methanol solution, it drives the equilibrium to the reactants and reduces the ester yield. Thus, the optimum methanol-to-oil molar ratio was 6:1.

#### 3.4. Stability and recycling of catalyst

Transesterification was completed under the following reaction conditions: reaction temperature, 65 °C; methanol-to-oil molar ratio, 6:1; catalyst amount, 2.0wt%; and reaction time, 2 h. The reaction mixture was centrifuged and separated to recover the wet

solid catalyst with methanol washing. Afterward, the catalyst was activated at 500 °C in the same muffle furnace for 3 h to remove adsorbed glycerol and methanol. The activated catalyst was subsequently used in the next cycle under the same reaction conditions as before. The reusability of the catalyst in the transesterification of soybean oil with methanol is shown in Fig. 9. The biodiesel yield decreased slightly after four runs, and the catalyst could be repeatedly used four times with biodiesel yield over 73.6%.

The decrease in catalytic activity after the fourth recycling may have been caused by two factors. One reason may be due to the reduced surface area which was caused by catalyst recalcination. The other reason may be the change in the morphology of the used catalyst. Particle aggregation of the catalyst after the third use was observed, which could be associated with its reduced catalytic activity. The leaching of K species into the biodiesel phase after the first run was determined using ICP–OES and listed in Table 4. The leaching of potassium species was only 4.0 mg/kg of biodiesel, which can satisfy the EN 14214 standards (below 5.0 mg/kg of biodiesel). Thus, the mixed snail shell and kaolin impregnated with KBr is a relatively reusable catalyst.

#### 3.5. Biodiesel component analysis

Results from the biodiesel component analysis are shown in Fig. 10. The reaction conditions were as follows: oil, 50 mL (45.6 g); methanol, 13 mL; reaction time, 2 h; reaction temperature, 65 °C; and catalyst, 0.92 g. Biodiesel was collected after the reaction for analysis. Table 3 and Fig. 10 show the appearance peak time and biodiesel component.

#### 3.6. Biodiesel properties

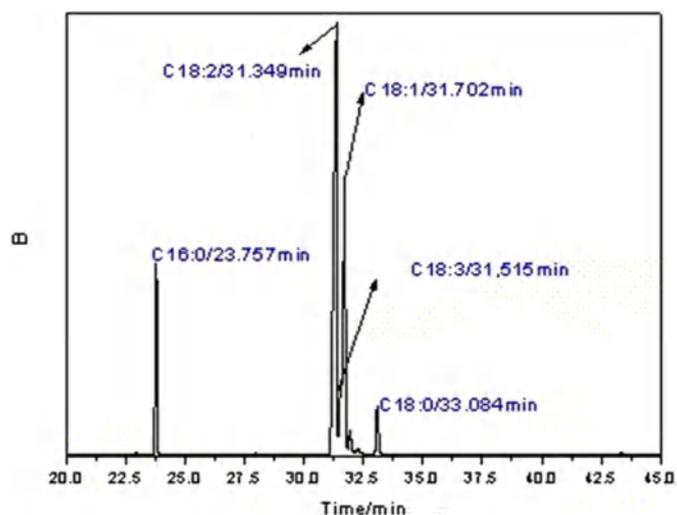
Table 4 shows the biodiesel physical and chemical properties produced under the following optimum conditions: activation temperature, 500 °C; activation time, 3 h; catalyst amount, 2.0 wt%; methanol-to-oil molar ratio, 6:1; reaction time, 2 h; and reaction temperature, 65 °C. Table 4 also shows a comparison of the obtained biodiesel with ASTM and EN 14214 standards. The produced biodiesel meets ASTM D 6751 standard limits. Thus, the properties of obtained biodiesel from the soybean oil are feasible as an alternative to diesel. It is an environmentally friendly fuel.

## 4. Conclusion

Using cost-effective and environment-friendly catalysts is particularly useful for biodiesel production. In this study, snail shell and kaolin were used as raw materials to prepare a catalyst impregnated with KBr and activated at 500 °C. The new catalyst showed high catalytic activities for the transesterification reaction.

**Table 4**  
Physical–chemical properties of the prepared biodiesel.

Property (units)	Measured value	ASTM D6751	EN 14214
Density (g/cm <sup>3</sup> , at 15 °C)	0.882 ± 0.003	0.870–0.890	0.860–0.900
Kinematic viscosity (mm <sup>2</sup> /s, at 40 °C)	4.32 ± 0.04	1.9–6.0	3.5–5.0
Flash point (°C)	156 ± 2	>130	>120
Copper strip corrosion (50 °C, 3 h)	1a	<No.3	<No.1
Ester content (%)	98.1 ± 0.9	–	>96.5
Moisture (%)	0.027 ± 0.002	<0.050	<0.050
Calorific value (kJ/kg)	39871	–	–
Total glycerin (%)	0.17 ± 0.01	<0.240	<0.250
Cold filter plugging point (°C)	–1.5 ± 1.0	–	–
Cloud point (°C)	–4.5 ± 1.0	–	–
Potassium content (mg/kg)	4.0 ± 0.2	–	<5.0



**Fig. 10.** GC–MS of biodiesel synthesized from transesterification of soybean oil in methanol using the new catalyst. Reaction conditions: oil 50 ml (45.6 g), methanol 13 ml, reaction time 2 h, reaction temperature 65 °C and catalyst 0.92 g.

The experimental results show that optimal solid catalyst preparation conditions were as follows: calcination temperature, 800 °C; KBr solution concentration, 40%; snail shell-to-kaolin mass ratio, 4:1; and activation temperature, 500 °C. When optimal catalyst was used in the transesterification of soybean oil to biodiesel, the highest biodiesel yield reached 98.5% under the following optimal conditions: catalyst amount, 2.0 wt%; methanol-to-oil molar ratio, 6:1; reaction time, 2 h; and reaction temperature, 65 °C. The catalyst could be recycled and reused four times without remarkable deactivation. Consequently, the prepared solid base catalyst (mixed snail and kaolin impregnated with KBr and activated at 500 °C) should have significant benefits over existing technologies because the synthesis of this catalyst is simple, environmentally friendly, and inexpensive. Additionally, a catalyst with high catalytic efficiency and reusability was obtained. Thus, the new catalyst can be regarded as a promising heterogeneous base catalyst candidate for industrial biodiesel production.

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