Utilization of waste freshwater mussel shell as an economic catalyst for biodiesel production

Shengyang Hu, Yun Wang, Heyou Han*

College of Science, State Key Laboratory of Agricultural Microbiology, Huazhong Agricultural University, Wuhan 430070, China

ARTICLE INFO

ABSTRACT

An economic and environmentally friendly catalyst derived from waste freshwater mussel shell (FMS) was prepared by a calcination-impregnation-activation method, and it was applied in transesterification of Chinese tallow oil. The as-prepared catalyst exhibits a "honeycomb" -like structure with a specific surface area of 23.2 $m^2\,g^{-1}$. The newly formed CaO crystals are major active phase of the catalyst. The optimal calcination and activity temperature are 900 °C and 600 °C, respectively. When the reaction is carried out at 70 °C with a methanol/oil molar ratio of 12:1, a catalyst concentration of 5% and a reaction time of 1.5 h, the FMS-catalyst is active for 7 reaction cycles, with the biodiesel yield above 90%. The experimental results indicate that the FMS can be used as an economic catalyst for the biodiesel production.

1. Introduction

Due to the exhaustion of fossil resources and the increasing emissions of pollutant, many studies have being directed towards the exploitation of alternative renewable fuel [1,2]. Biodiesel, as a potential substituted energy, has attracted great attentions in recent years [3,4]. However, the high production cost of biodiesel compared with that of diesel fuel derived from petroleum limits its development. An important contribution to the high production cost results from the catalytic transesterification reaction [5]. Current biodiesel manufacturing processes primarily employs homogeneous strong bases [6,7] or acids [8,9] as catalysts due to their high activity and conversion. However, the separation of catalyst and the purification of products are time consuming and expensive accompanied with a large volume of chemical wastewater [10,11].

In order to circumvent most of the economical and environmental drawbacks of homogeneous process, heterogeneous catalysts, which can be easily separated from reaction mixture by filtration or centrifugation and reused for several runs, have been studied intensively. These catalysts are less corrosive, safer, and more environment-friendly [12]. At the laboratory scale, several heterogeneous catalysts, such as alkali and alkali earth metal oxides [13−17], cation-exchange resin [18], zeolites [19] and magnesium−aluminium mixed oxides [20,21], have been developed for biodiesel production. Unfortunately, the synthesis of highly active heterogeneous catalysts is complex, costly, and requires special skills to operate. Therefore, it is a great challenge to explore an ideal solid basic catalyst that is highly effective, low-cost, and ecologically friendly for the promising biodiesel production.

To address the issues, utilization of natural calcium sources from waste shells as an economic catalyst has been a new trend for biodiesel production. Nakatani et al. [22] examined transesterification of soybean oil catalyzed by combusted oyster shell. The research demonstrated that the biodiesel yield was more than 70% under the optimized reaction

* *Corresponding author.* Tel./fax: +86 27 87288246.
  E-mail address: hyhan@mail.hzau.edu.cn (H. Han).

conditions of a catalyst concentration and reaction time of 25 wt.% and 5 h, respectively. Wei et al [23]. and Boey et al [24]. reported that eggshell and crab shell can be utilized as a catalyst for biodiesel production, respectively. Recently, Vieiya-empikul et al [25]. also investigated the catalytic behaviors of golden apple snail shell and meretrix venus shell for the methyl ester production from palm oil. These catalysts derived from waste shell exhibit large potential for biodiesel production due to low-cost and environment-friendly characteristics.

Freshwater mussel is an aquatic bivalve mollusk and is similar to their marine clam and oyster. It has two shells connected by a hinge-like ligament. The freshwater mussel generally inhabits rivers, lakes and ponds. In China, for example, it is estimated that the annual production of freshwater mussel is over 1.6 million tons (including shell weight) in 2007, resulting in the production of much FMS waste. A large part of waste shell is commonly disposed in the field without any pretreatment, giving a potential threat to arable farmers. In order to reduce the amount of FMS waste, a great deal of effort has been conducted for the application of shell as value-added products. Until now, the application has been limited to a low-cost adsorbent for extracting metal ions [26] and a desulphurization agent to remove SO_2 [27]. The inorganic constituent of FMS is mainly calcium carbonate (ca. 95%), which may assume either of two principal crystalline forms, calcite and aragonite. The calcium-rich shell is easily converted into calcium oxide by high-temperature calcination in air. Therefore, it is possible to utilize calcined FMS as a low-cost solid catalyst for biodiesel production.

The present studies aimed at exploring the possibility of utilizing FMS waste as a catalyst in catalytic process of bio-diesel production. Scanning electron microscope (SEM) and X-ray diffractometer (XRD) were employed to characterize the microstructures and crystalline phase of catalyst. Thermogravimetric analysis (TGA) was used to determine the suitable calcination and activation temperature. The catalytic behavior was evaluated by transesterification of Chinese tallow oil (CTO) and methanol. The influence of various experimental variables, such as calcination temperature and activation temperature, on the catalytic activity was also investigated.

2. Experimental

2.1. Materials

FMS was collected as waste from the local field. The shell was rinsed with water and dried in a 105 °C oven. Inedible Chinese tallow oil was obtained from Dawu County, Hubei province. The fatty acid composition consists of 0.21% myristic acid, 7.51% palmitic acid, 2.60% stearic acid, 16.50% oleic acid, 32.75% linoleic acid, 39.36% linolenic acid and traces of other acids. The analytical grade methanol was purchased from Zhenxing Chemical Co. (Shanghai).
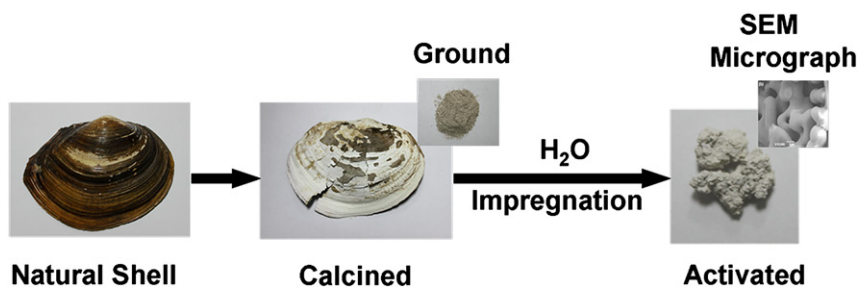
2.2. Catalysts preparation

FMS - catalyst was prepared by calcination-impregnation-activation method. Scheme 1 illustrated the preparation process of FMS - catalyst. The dried FMS was calcined at 200—1000 °C in a muffle furnace after being ground to 200—400 microns. Those FMS calcined at 900 °C for 4 h (quoted as FMS-900) was completely impregnated in deionized water and then was activated at 600 °C for 3 h. The resultant material was called FMS - catalyst (quoted as FMS-900-600).

2.3. Catalysts characterization

The thermal stability of FMS-catalyst was examined using NETZSH TG 209C from room-temperature to 900 °C under an inert nitrogen atmosphere and a heating rate of 10 °C min^{-1}. XRD analysis was carried out with a Rigaku D/MAX-RB diffractometer under the following conditions: FeKα radiation ($\lambda = 1.9373$ Å), tube voltage of 36 kV, a tube current of 20 mA and the count time of 0.2 s per 0.02° in the range of 15—90°. SEM micrographs were obtained on a JEOL JSM-6390 to observe the morphology of samples. BET was measured with a Quantach-rome Autosorb-1-C chemisorption—physisorption analyzer. Laser Raman spectroscopic measurements were performed on a Renishaw invia Raman spectrometer equipped with an intergral microscope (Olympus). The excitation source was Ar laser (633 nm), focused with a 50 × long-local-length objective microscope and providing a power of 20 mW on the sample.

2.4. Reaction procedure

The transesterification was performed using different catalyst concentration and molar ratio of methanol to oil. All experiments were carried out in a 100 mL glass reactor equipped with a condenser and a mechanical stirrer. It was charged with 25 g Chinese tallow oil (molecular mass was ca. 896 g mol^{-1}) and varied amounts of anhydrous methanol and catalyst. The mixture was refluxed at 70 °C, with mechanical stirring for a specified time. After the reaction, the catalyst was separated by filtration. The content of fatty acid methyl

Scheme 1 — Preparation procedure of catalyst derived from FMS.

Table 1 – Levels of for the central composite design.

Variables	Symbols	Real values of coded levels				
		$-\alpha$	-1	0	$+1$	$+\alpha$
Catalyst concentration (wt.%)	X_1	3.59	4	5	6	6.41
Molar ratio of methanol to oil	X_2	7.76:1	9:1	12:1	15:1	16.24:1

ester in samples was analyzed in similar method reported by Kansedo et al. [28]. Column temperature and temperature program were set as follows: the initial temperature was set at 190 °C, and then was increased to 280 °C with a rate of 10 °C min^{-1}. The temperatures of the injector and detector were set at 300 and 280 °C, respectively. The flow velocity of H$_2$, N$_2$ and air were kept at 40, 25 and 400 mL min^{-1} .The yield of biodiesel was calculated according to the method reported by He et al. [29].

2.5. Statistical design for experimental

The experimental design in the present study is a central composite design, where the catalyst concentration and molar ratio of methanol to oil are selected as variables. The central composite design (CCD) consists of 13 experiments with four factorial points, five central points and four axial points. The distance of the axial points encoded $+\alpha$ and $-\alpha$ from the center point is $\alpha = 2^{k/4}$, where k is the number of independent variables. The independent variables and their levels in coded and actual values are shown in Table 1. The experimental matrix for the central composite design is summarized in Table 2. All experiments are conducted in a random order. Experimental data is analyzed with software SAS version 8.1 (SAS Institute Inc., Cary, NC, USA). The association between dependent and independent

variables in present study is explained by the following second-order polynomial model:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_1^2 + \beta_4 X_1 X_2 + \beta_5 X_2^2 \quad (1)$$

where Y is the dependent variable (biodiesel yield); X_1 and X_2 are the independent variables; β_0, β_1, β_2, β_3, β_4 and β_5 are intercept, linear, quadratic and interaction constant coefficients, respectively.

3. Results and discussion

3.1. Characterization of FMS-catalyst

Fig. 1 shows the TGA curves of natural shell, FMS-900 and FMS-900-600. For the natural shell (curve c), at a temperature lower than 380 °C (1st stage), there is ca. 3.1% weight loss owing to the removal of organics and evaporation of moisture by physisorption and chemisorption. When the temperature is above 380 °C, the crystalline phase of CaCO$_3$ is transformed from aragonite to calcite. A weight loss of 0.8% is recorded in the temperature range of 380–464 °C (2nd stage). The major weight loss (41.3%) occurs in the temperature range of 631–765 °C (3rd stage), which is attributed to the decomposition of CaCO$_3$. When the calcination temperature is above 800 °C, the weight loss remains almost constant. Therefore, the suitable calcination temperature is above 800 °C to transform CaCO$_3$ to CaO. Compared with TGA curve of FMS-900, there are two new weight lost peaks in TGA curve of FMS-900-600. One at 339–465 °C, corresponded to the release of H$_2$O molecular derived from decomposition of Ca(OH)$_2$ and incidental formation of "honeycomb" -like structure, which is accompanied by a weight loss of 23.5%. And another at 560–637 °C which is attributed to phase transition of CaO [30] and there is only a weight loss of 1.4%. As presented in TGA curve of FMS-900-600, 500 °C should be the temperature high enough for full decomposition of Ca(OH)$_2$. In fact, a higher activation temperature is required to enhance the catalytic activity of catalyst. It was proved by the subsequent experimental results.

The FMS - catalyst was further probed by XRD (Fig. 2). The composition of FMS-catalyst is two principal crystalline CaCO$_3$, calcite and aragonite (JCPDS card NO. 29-0306 and
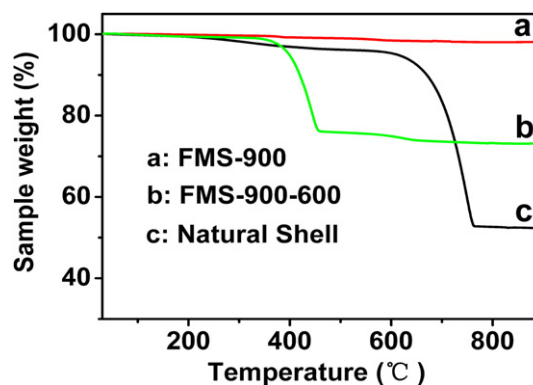
Table 2 – Experimental matrix and experimental results for the central composite design.

Run no.	Type	Variables		Coded variables		Response Y (%)
		C	M	X_1	X_2	
1	Factorial	4	9:1	-1	-1	62.4
2	Factorial	4	15:1	-1	$+1$	85.9
3	Factorial	6	9:1	$+1$	-1	73.5
4	Factorial	6	15:1	$+1$	$+1$	95.4
5	Center	5	12:1	0	0	95.5
6	Center	5	12:1	0	0	95.0
7	Center	5	12:1	0	0	96.2
8	Center	5	12:1	0	0	94.7
9	Center	5	12:1	0	0	94
10	Axial	6.41	12:1	$+\alpha$	0	93.2
11	Axial	5	16.24:1	0	$+\alpha$	95.8
12	Axial	5	7.76:1	0	$-\alpha$	60.1
13	Axial	3.59	12:1	$-\alpha$	0	78.6

Fig. 1 – TGA profiles of catalysts before (a) and after (b) impregnation, and natural shell (c).
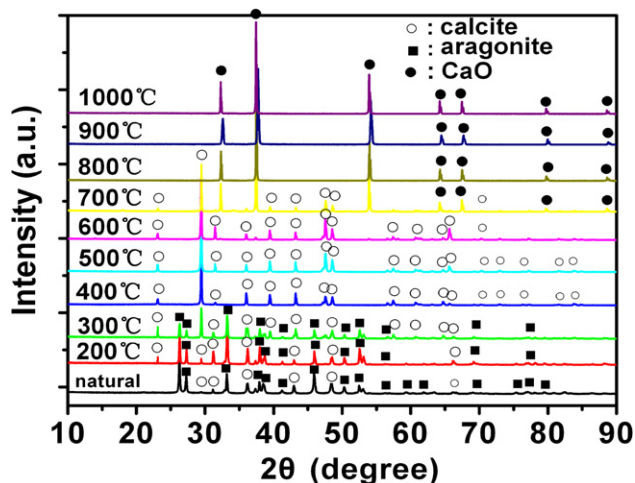
Fig. 2 − XRD patterns of natural shell and catalysts obtained by calcining natural shell between 200−1000 °C.

Fig. 3 − Raman spectra of natural shell, pure CaCO₃, and catalysts obtained by calcining natural shell at 400, 700, 900 °C.

41-1475) when the FMS-catalyst is calcined at a temperature lower than 400 °C. The diffraction patterns of FMS-catalyst calcined at the temperature range of 400−600 °C are characteristic of calcite. When the calcination temperature is above 800 °C, the diffraction patterns of FMS-catalyst are characteristic of CaO (JCPDS card NO. 82-1691), caused by the decomposition of CaCO₃ from the natural shell. While the FMS-catalyst calcined at 700 °C contains calcite as the major phase and CaO as a minor phase.

Fig. 3 presents the Raman spectra of FMS calcined at different temperatures. For natural shell (curve a), the vibration bands of 711.7 and 1085.8 cm^{-1} correspond to CaCO₃, according to the standard Raman spectra of CaCO₃

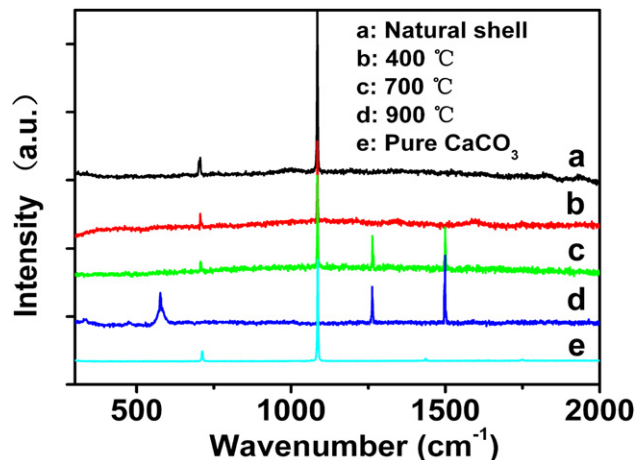(curve e). Curves b−d show the Raman spectra of catalysts calcined at 400 °C, 700 °C and 900 °C, respectively. Obviously, the Raman spectra of catalyst calcined at 400 °C is similar to that of natural shell (curve a). While the FMS-catalyst calcined at 900 °C displays the vibration bands of CaO (1263.1, 1499.9 cm^{-1}) (curve d), according to the standard Raman spectra of CaO (unshown). When the catalyst is calcined at 700 °C, the vibration bands of CaCO₃ and CaO are observed in the same Raman spectrum. The results are well consistent with those of XRD.

The morphology of FMS calcined at different temperature was examined by SEM (Fig. 4). The natural shell displays a typical layered architecture [31]. With the calcination
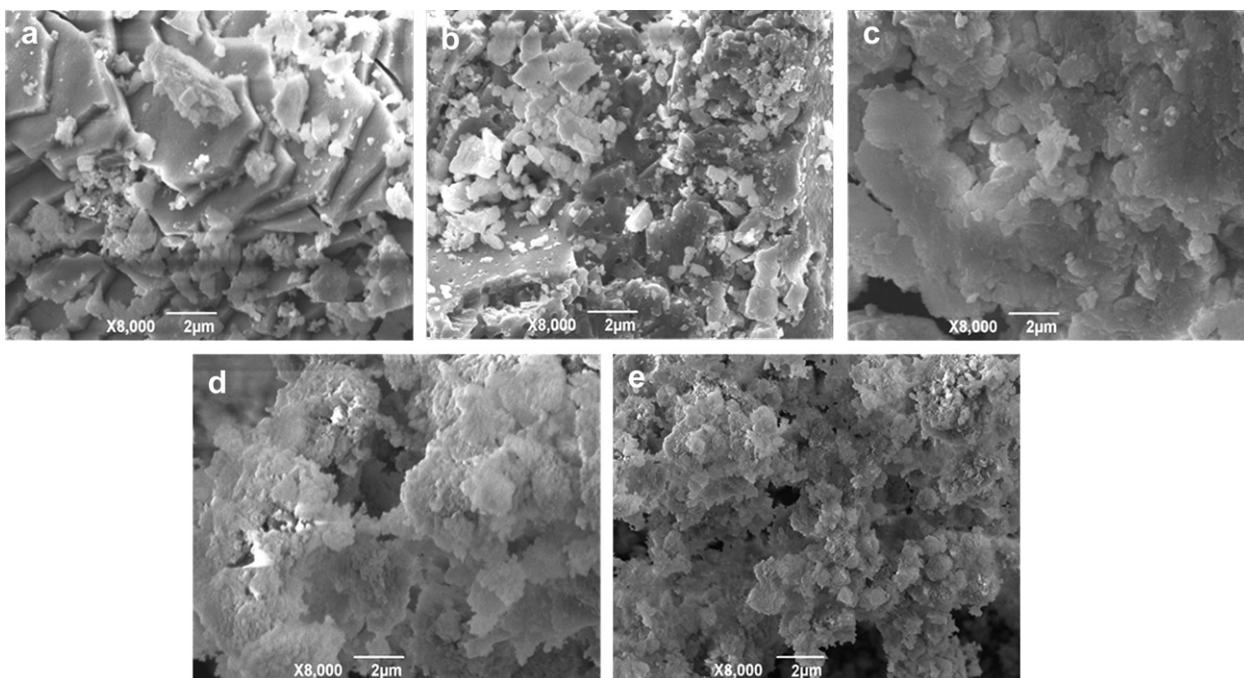

Fig. 4 − SEM images of natural shell, and catalysts obtained by calcining natural shell at 400, 700, 900 °C.

Table 3 — BET surface area (S_{BET}) and catalytic activity of FMS-catalyst

Catalyst	S_{BET} (m^2g^{-1})	Yield (%)
Lab-CaO[a]	4.5	92
Natural shell	0.9	No reaction
FMS-900	1.5	71%
FMS-900-600	23.2	96%

a Laboratory CaO was calcined at 600 °C.

Fig. 6 — The influence of molar ratio of methanol to oil on biodiesel yield. Catalyst concentration: 4%; reaction temperature: 70 °C.

temperature rising from 200 to 900 °C, the microstructures of natural shell are changed significantly from layered architecture to porous structure. When the FMS-900 is further impregnated in deionized water and then activated at 600 °C, the resultant catalyst (FMS-900-600) shows a " honeycomb " -like porous surface (Fig. 4e). This is probably due to the fact that a large number of gaseous water molecular from the decomposition of Ca(OH)$_2$ is released from catalyst. The gaseous water molecular creates high porosity, i.e. they act as porogens in the catalyst. During preparation process of catalyst, the specific surface area also is different obviously (Table 3). Among the catalysts, the FMS-900-600 exhibits the largest specific surface area (23.2 m^2 g^{-1}). The both steps of impregnation and activation play an important role in improving specific surface of catalyst. It is evident that large specific surface results in high catalytic activity. As also summarized in Table 3, the activity of catalysts decreases in the order FMS-900-600 > CaO > FMS-900 > natural shell.

3.2.   Influence of preparation conditions on catalytic activity

To investigate the influence of preparation conditions on catalytic activity, a series of catalysts were prepared at different conditions, including calcination and activity temperature, and they were used for transesterification of Chinese tallow oil and methanol. Fig. 5a demonstrates the results concerning influence of calcination temperature on the catalytic activity. The catalysts calcined below 600 °C almost have no catalytic activity. And a yield of ca.60% is obtained at 700 °C. When the calcination temperature is above 800 °C, the biodiesel yield is 71%. In terms of energy consumption, the calcination temperature of 900 °C is
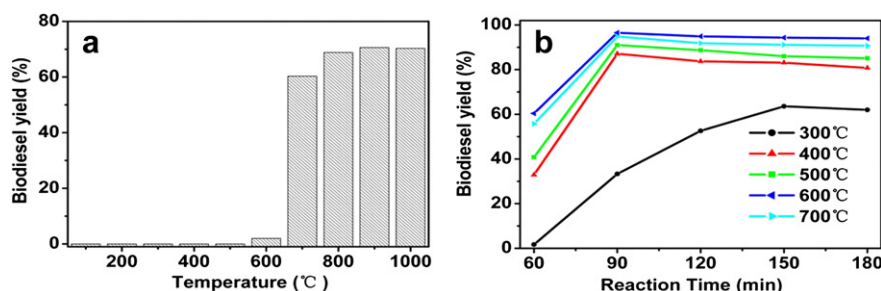
appropriate to transform fully calcium carbonate to calcium oxide. However, the FMS calcined at 900 °C (FMS-900) is further impregnated in deionized water and then is activated at 600VC. A higher yield of 96% is achieved under follows reaction: a molar ratio of methanol to oil of 12:1, a catalyst concentration of 5 wt.% and a reaction temperature of 70 °C for 1.5 h (Fig. 5b). Compared to the published literature [22], the catalyst concentration and reaction time are reduced obviously. The high catalytic activity is also explained by the BET surface area of 23.2 m^2 g^{-1} for FMS-900-600 versus only 10.5 m^2 g^{-1} for FMS-900. According to our experiment results, the appropriate activity temperature should be 600 °C.

3.3.   Influence of single variable on biodiesel yield

The effect of single variable on the biodiesel yield, such as catalyst concentration and molar ratio of methanol to oil, were examined. For the following experiments, FMS-900-600 was used as low-cost catalyst to catalyze the trans-esterification of Chinese tallow oil and methanol.

The molar ratio of methanol to oil is an important variable affecting the yield of biodiesel. The stoichiometric molar ratio of methanol to oil for transesterification is 3:1. In practice, the molar ratio should be higher in order to drive the reaction

Fig. 5 — The influence of (a) calcination temperature; (b) activation temperature on catalytic behavior. Molar ratio of methanol to oil:12:1; catalyst concentration: 5%; reaction temperature: 70 °C; reaction time 1.5 h.
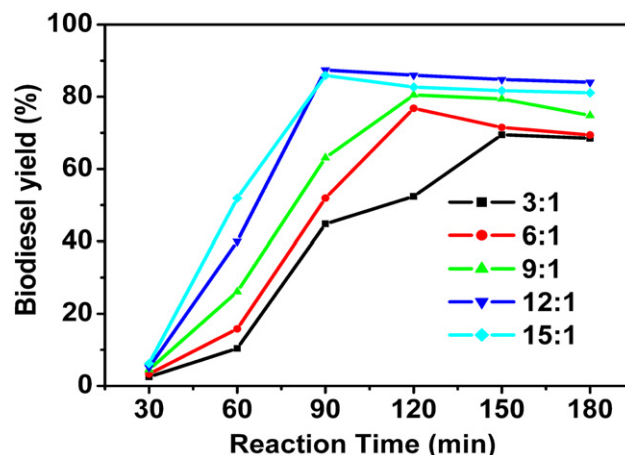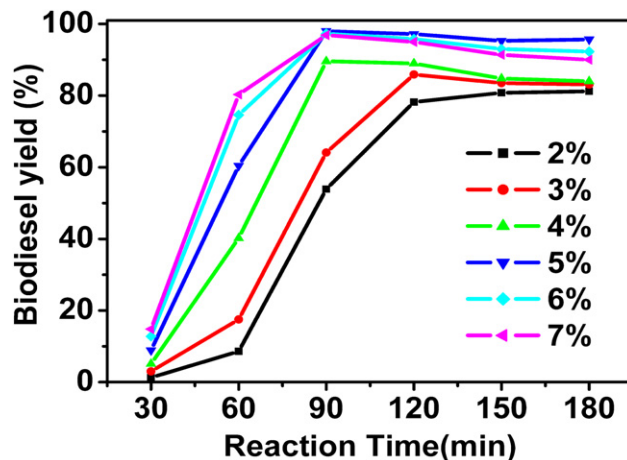
Fig. 7 – The influence of catalyst concentration on biodiesel yield. Molar ratio of methanol to oil:12:1; reaction temperature: 70 °C.

towards completion and gain more products. Fig. 6 describes the influence of the molar ratio on the yield of biodiesel. The yield of transesterification initially increased with the increase of methanol/oil molar ratio, and then reached a maximum of 88% at 12:1. When the molar ratio exceeded 12:1, the yield remained nearly constant. The excessive methanol is helpful for full contact of reagents and catalyst, so as to accelerate the reaction rate. However, a higher molar ratio of methanol to oil is not favorable for the purification of product in the following separation process. Also, recovery of the excessive methanol will consume large amounts of energy. Therefore, a methanol/oil molar ratio of 12:1 is adopted in our experiment.

Another key parameter to be optimized is the catalyst concentration. Fig. 7 exhibits the results regarding the influence of catalyst concentration on the yield of biodiesel. Experimentally, the yield varies proportionately to the catalyst concentration. A maximum yield of 96% is obtained at a catalyst concentration of 5 wt.%. However, the yield does not increase when the concentration is above 5 wt.%. Getting the reactants to and from the catalyst become the rate determining step (mass transport limitation) which is why adding more catalyst is not favorable for increase of biodiesel yield [23]. Thus, the optimal catalyst concentration should be 5 wt. % in this system.

3.4. Statistical analysis

The experimental results corresponding to the central composite design are also shown in Table 2. The RSREG procedure from SAS is employed to fit the polynomial Eq. (1) to the experimental data. The obtained regression model in terms of the coded variables is given in Eq. (2)

$$Y = 94.88 + 5.16X_1 + 11.99X_2 - 5.15X_1^2 - 0.40X_1X_2$$
$$- 9.12X_2^2(R^2 = 99.05\%) \tag{2}$$

The fitted model is analyzed using analysis of variance (Table 4), where the P-values are applied to establish the corresponding coefficient significance. The P-value of model is very low (<0.0001), indicating the second-order polynomial regression model is highly significant. The determination coefficient (R^2) is shown as 0.9905, which demonstrates that the accuracy and general availability of the polynomial model are very good, and the response trends can be analyzed compatibly and well by the model. The coefficient values of the regression equation are listed in Table 5. The results reveal that the catalyst concentration is the most important variable in the biodiesel yield response, followed by the molar ratio of methanol to oil. Both variables have a positive effect on the yield of biodiesel. However, the interaction between the catalyst concentration the molar ratio of methanol to oil is insignificant.

Table 4 – Analysis of variance for the fitted second-order polynomial model.

Source	DF	Sum of squares	F Value	Pr > F
Linear	2	1361.960228	242.11	<0.0001
Quadratic	2	689.590963	122.59	<0.0001
Cross-product	1	0.640000	0.23	0.6479
Total model	5	2052.191191	145.92	<0.0001
Lack of fit	3	16.980809	8.36	0.0338
Pure error	4	2.708000		
Total error	7	19.688809		
$R^2 = 99.05\%$				

Table 5 – Results of regression analysis for a full second-order polynomial model.

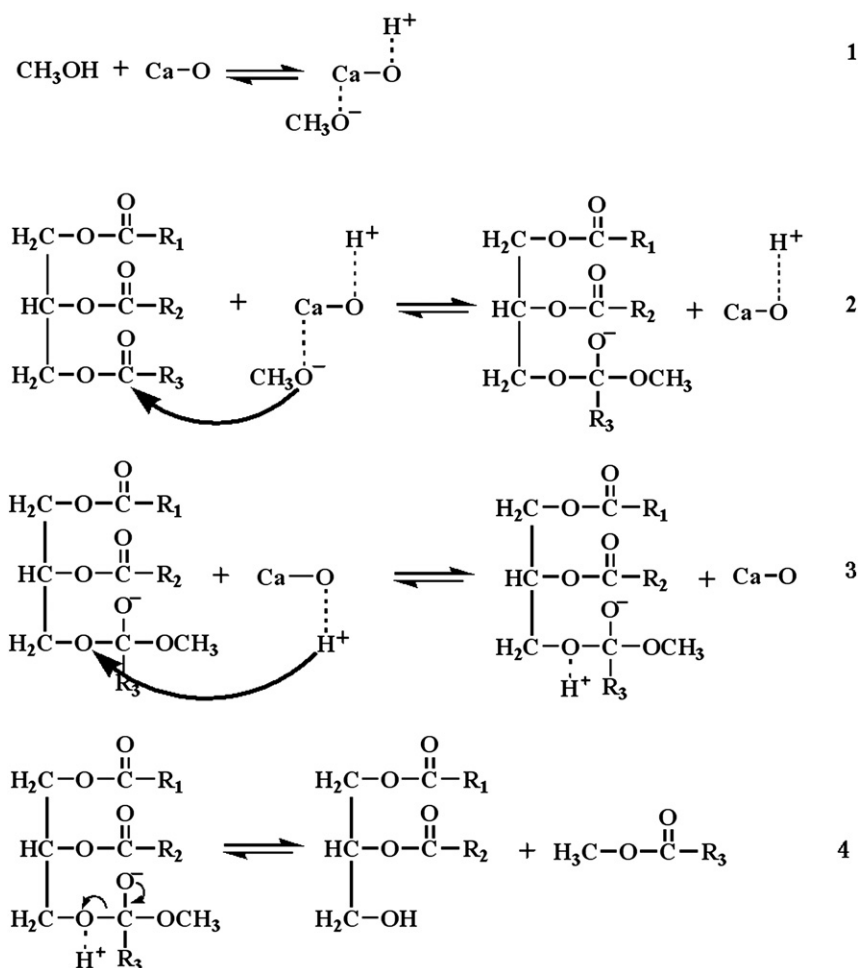| Term	DF	Coefficient	t-value	Pr > F
Intercept	1	94.880317	126.50	<0.0001
$\beta 1$	1	5.156329	8.70	<0.0001
$\beta 2$	1	11.986785	20.21	<0.0001
$\beta 3$	1	−5.146984	−8.09	<0.0001
$\beta 4$	1	−0.400000	−0.48	0.6479
$\beta 5$	1	−9.123185	−14.34	<0.0001

Fig. 8 – Mechanism of FMS catalyst catalyzed transesterification.

The response surface corresponding to the regression model (Eq. (2)) is shown in Fig. 10, which exhibits the effects of two independent variables on the biodiesel yield. From a response surface plot, the optimal reaction conditions for the catalyst concentration and molar ratio of methanol to oil are 5.3 wt.% and 13.4:1, respectively. Under the optimal reaction conditions, the theoretical biodiesel yield obtained from the second-order polynomial regression model (Eq. (2)) is 99.8%. The accuracy of the model is validated with triplicate experiments under the aforementioned optimal reaction conditions. The experimental yield of biodiesel is 97.5%, which is in close agreement to the theoretical yield, indicating the model has a high predictive ability.

3.5. Catalytic mechanism

CaO is major active phase of FMS-catalyst. Fig. 8 shows the possible mechanism of catalyst in transesterification reactions. The formation of the methoxide anion is the first step of the reaction, arising from the reaction between CaO and methanol (step 1). Next, the methoxide anion attacks the carbonyl carbon of triglyceride to form an alkoxycarbonyl intermediate (step 2). The alkoxycarbonyl intermediate contests subsequently a hydrogen proton derived from

CaO–H $^+$, producing CaO and another alkoxycarbonyl intermediate (step 3). Finally, the intermediate rearranges and divides into biodiesel (methyl ester) and diglyceride (step 4) [32].
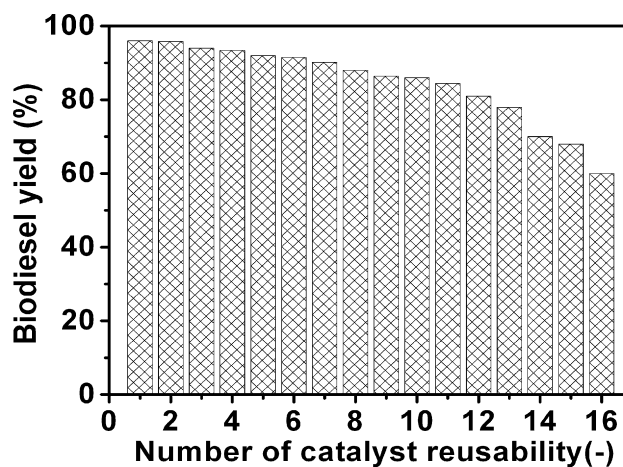

Fig. 9 – Reusability performance of catalyst derived from FMS in the transesterification reaction. Molar ratio of methanol to oil:12:1; catalyst concentration: 5%; reaction temperature: 70 °C; reaction time 1.5 h.
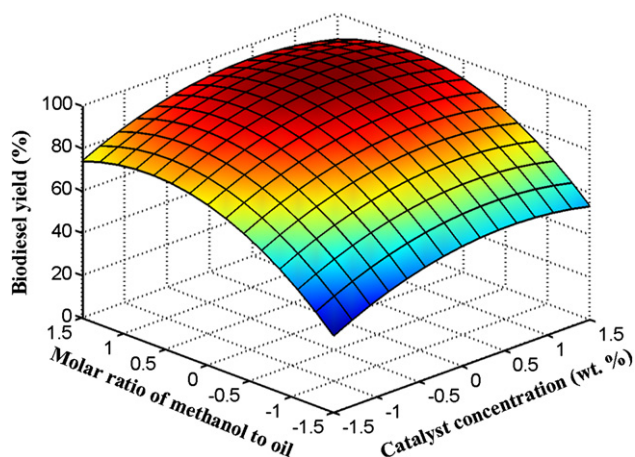
Fig. 10 — Response surface plot of the second-order polynomial model for biodiesel yield as a function of catalyst concentration and molar ratio of methanol to oil.

3.6.   Deactivation and reusability of FMS - catalyst

The reusability of the catalyst is examined by carrying out reaction cycles. When transesterification reaction finished, the catalyst is separated from the mixture and used again without any subsequent treatment in a second reaction under the same conditions as before. It is found the prepared catalyst is active for 7 reaction cycles, with yield above 90%. After 12 reaction cycles, the biodiesel yield lowers to 80% (Fig. 9). Catalyst deterioration is probably due to the change of catalyst surface structure. Calcium oxide is transformed to calcium hydroxide gradually due to the moisture in the reactants, which deteriorate the activity of catalyst [5,33]. However, the activity can be recovered after calcination in air at 600 °C.

4.   Conclusions

A low-cost and environmentally friendly catalyst derived from FMS was utilized success fully for biodiesel production. The FMS is firstly calcined at 900 °C to transform calcium carbonate to calcium oxide, then those calcined shell is completely impregnated in deionized water and it is activated subsequently at 600 °C. After the three steps, the catalyst performs the optimal catalytic activity. Measurement results of XRD and Raman reveal that the newly formed CaO crystals are major active phase of the catalyst. Characterization results of TEM and BET indicate that the FMS -derived catalyst has a "honeycomb" -like porous structure with a large specific surface area ($23.2 \, m^2 \, g^{-1}$). The both steps of impregnation and activation play an important role in the increase of specific surface of catalyst. When the reaction is carried out at 70 °C with a methanol/oil molar ratio of 12:1, a catalyst concentration of 5 wt.% and a reaction time of 1.5 h, the FMS-catalyst is active for 7 times of reuse, with the biodiesel yield above 90%. Application of the FMS -derived catalyst for biodiesel production can effectively reduce biodiesel integrated production cost, making it competitive with petroleum-derived diesel.

REFERENCES

[1] Alba-Rubio AC, Santamaría-González J, Mérida-Robles JM, Moreno-Tost R, Martín-Alonso D, Jiménez-López A, et al. Heterogeneous transesterification processes by using CaO supported on zinc oxide as basic catalysts. Catal Today 2010; 149:281—7.
[2] Sun H, Ding Y, Duan J, Zhang Q, Wang Z, Lou H, et al. Transesterification of sunflower oil to biodiesel on ZrO_2 supported $La_2 \, O_3$ catalyst. Bioresour Technol 2010;101: 953—8.
[3] Lin CY, Lin HA, Hung LB. Fuel structure and properties of biodiesel produced by the peroxidation process. Fuel 2006;85: 1743—9.
[4] Di Serio M, Tesser R, Lu P, Santacesaria E. Heterogeneous catalysts for biodiesel production. Energy Fuels 2008;22: 207—17.
[5] López Granados M, Zafra Poves MD, Martín Alonso D, Mariscal R, Cabello Galisteo F, Moreno-Tost R, et al. Biodiesel from sunflower oil by using activated calcium oxide. Appl Catal B 2007;73:317—26.
[6] Rashid U, Anwar F, Moser BR, Ashraf S. Production of sunflower oil methyl esters by optimized alkali-catalyzed methanolysis. Biomass Bioenerg 2008;32:1202—5.
[7] Siler-Marinkovic S, Tomasevic A. Transesterification of sunflower oil in situ. Fuel 1998;77:1389—91.
[8] Di Serio M, Tesser R, Dimiccoli M, Cammarota F, Nastasi M, Santacesaria E. Synthesis of biodiesel via homogeneous Lewis acid catalyst. J Mol Catal A Chem 2005;239:111—5.
[9] Aranda DAG, Santos RTP, Tapanes NCO, Ramos ALD, Antunes OAC. Acid-catalyzed homogeneous esterification reaction for biodiesel production from palm fatty acids. Catal Lett 2008;122:20—5.
[10] Zhang Y, Dubé MA, McLean DD, Kates M. Biodiesel production from waste cooking oil: 2. Economic assessment and sensitivity analysis. Bioresour Technol 2003;90:229—40.
[11] Vicente G, Martínez M, Aracil J. Integrated biodiesel production: a comparison of different homogeneous catalysts systems. Bioresour Technol 2004;92:297—305.
[12] Kim HJ, Kang BS, Kim MJ, Park YM, Kim DK, Lee JS, et al. Transesterification of vegetable oil to biodiesel using heterogeneous base catalyst. Catal Today 2004;93-95:315—20.
[13] Gryglewicz S. Alkaline-earth metal compounds as alcoholysis catalysts for ester oils synthesis. Appl Catal A Gen 2000;192:23—8.
[14] Ebiura T, Echizen T, Ishikawa A, Murai K, Baba T. Selective transesterification of triolein with methanol to methyl oleate and glycerol using alumina loaded with alkali metal salt as a solid-base catalyst. Appl Catal A Gen 2005;283:111—6.
[15] Liu X, He H, Wang Y, Zhu S. Transesterification of soybean oil to biodiesel using SrO as a solid base catalyst. Catal Commun 2007;8:1107—11.
[16] Gryglewicz S. Rapeseed oil methyl esters preparation using heterogeneous catalysts. Bioresour Technol 1999;70:249—53.
[17] Venkat Reddy CR, Oshel R, Verkade JG. Room-temperature conversion of soybean oil and poultry fat to biodiesel catalyzed by nanocrystalline calcium oxides. Energy Fuels 2006;20:1310—4.

[18] Feng Y, He B, Cao Y, Li J, Liu M, Yan F, et al. Biodiesel production using cation-exchange resin as heterogeneous catalyst. Appl Catal A Gen 2010;101:1518–21.

[19] Suppes GJ, Dasari MA, Doskocil EJ, Mankidy PJ, Goff MJ. Transesterification of soybean oil with zeolite and metal catalysts. Appl Catal A Gen 2004;257:213–23.

[20] Xie W, Peng H, Chen L. Calcined Mg-Al hydrotalcites as solid base catalysts for methanolysis of soybean oil. J Mol Catal A Chem 2006;246:24–32.

[21] Gao L, Teng G, Lv J, Xiao G. Biodiesel synthesis catalyzed by the KF/Ca–Mg–Al Hydrotalcite base catalyst. Energy Fuels 2010;24:646–51.

[22] Nakatani N, Takamori H, Takeda K, Sakugawa H. Transesterification of soybean oil using combusted oyster shell waste as a catalyst. Bioresour Technol 2009;100:1510–3.

[23] Wei Z, Xu C, Li B. Application of waste eggshell as low-cost solid catalyst for biodiesel production. Bioresour Technol 2009;100:2883–5.

[24] Boey PL, Maniam GP, Hamid SA. Biodiesel production via transesterification of palm olein using waste mud crab (*Scylla serrata*) shell as a heterogeneous catalyst. Bioresour Technol 2009;100:6362–8.

[25] Viriya-empikul N, Krasae P, Puttasawat B, Yoosuk B, Chollacoop N, Faungnawakij K. Waste shells of mollusk and egg as biodiesel production catalysts. Bioresour Technol 2010;101:3765–7.

[26] Tudor HEA, Gryte CC, Harris CC. Seashells: detoxifying agents for metal-contaminated waters. Water Air Soil Pollut 2006;173:209–42.

[27] Cheng S, Wei E, Shi Z, Luo Z, Cen K. Experimental studies on shells desulphurization in fluidized bed combustion. Chin a Environ Sci 2002;22:309–12.

[28] Kansedo J, Lee KT, Bhatia S. Biodiesel production from palm oil via heterogeneous transesterification. Biomass Bioenerg 2009;33:271–6.

[29] He HY, Wang T, Zhu SL. Continuous production of biodiesel fuel from vegetable oil using supercritical methanol process. Fuel 2007;86:442–7.

[30] Deng Y, Jia OH, Chen XR, Zhu J. Phase transition and elastic constants of CaO from first-principle calculations. Physica B 2007;392:229–32.

[31] Geist J, Auerswald K, Boom A. Stable carbon isotopes in freshwater mussel shells: environmental record or marker for metabolic activity? Geochim Cosmochim Acta 2005;69:3545–54.

[32] Kouzu M, Kasuno T, Tajika M, Sugimoto Y, Yamanaka S, Hidaka J. Calcium oxide as a solid base catalyst for transesterification of soybean oil and its application to biodiesel production. Fuel 2008;87:2798–806.

[33] Kouzu M, Kasuno T, Tajika M, Yamanaka S, Hidaka J. Active phase of calcium oxide used as solid base catalyst for transesterification of soybean oil with refluxing methanol. Appl Catal A Gen 2008;334:357–65.