

# NaOH-impregnated oyster shell as a solid base catalyst for transesterification of soybean oil

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**Abstract:** There is a significant interest in developing renewable solid base catalysts from agricultural wastes for the use in the transesterification of fats into fatty acid methyl esters (FAME). In this study, an inexpensive base catalyst was synthesized by impregnating waste oyster shell with 50% sodium hydroxide solution, followed by calcination at 1000°C for 3 h. The resulting solid catalyst was used to catalyze transesterification of soybean oil. Transesterification using the catalyst was studied by systematically varying molar ratio (MR) (methanol to oil) and catalyst loading (CL). Results indicated that the highest FAME yield was 93.9% using MR of 12 and CL of 10%. Reusability tests suggested that the catalyst could be used for at least three runs without any significant decrease in FAME yield.

**Keywords:** fatty acid methyl esters, biodiesel, transesterification, oyster shell, reusability

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## 1 Introduction

The decreasing production and environmental issues associated with fossil fuels are compelling researchers and scientists to explore other sources of energies that are renewable, practical, and easy to produce.

Biodiesel, or fatty acid methyl esters (FAMES), is one such biomass-derived and renewable fuel. As a fuel, biodiesel has excellent lubricating properties and cetane ratings compared with diesel fuels (Atabani et al., 2012).

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Presently, biodiesel is being used as a fuel for public transportation, including cars, trains, and aircraft. Biodiesel may be produced via thermochemical (e.g., pyrolysis), biochemical (e.g., fungal fermentation), and catalytic (e.g., transesterification) (Ma and Hanna, 1999) processes, although transesterification is the most widely used method for biodiesel production in the industry.

Transesterification is a chemical reaction that converts a carboxylic acid ester into another one (Quader and Ahmed, 2017). In the case of biodiesel production, triglycerides from oil react with methanol or ethanol to produce glycerol and FAMES, which are further modified to biodiesel. A catalyst is usually needed for transesterification to ensure a high reaction rate since non-catalytic transesterification usually requires extremely high reaction temperature and

methanol content (Diasakou et al., 1998). Homogeneous base catalysts, such as sodium hydroxide or potassium hydroxide, are usually employed to catalyze the reaction. However, homogeneous base catalysts usually result in a series of problems, including issues with catalyst recovery, large wastewater production, and corrosion to operation facilities, all of which increase the production cost of biodiesel. Heterogeneous base catalysts can solve these problems because they are easily separated and reused, less corrosive to facilities, and reduce wastewater production (Kawashima et al., 2008). Hence, alkaline earth metal oxides, such as MgO, CaO, and SrO, have been tested for transesterification of refined oil (Liu et al., 2007; Liu et al., 2008; Yacob et al., 2009). Both CaO and SrO provided biodiesel yields of over 95%, while MgO provided a biodiesel yield of about 51.3%, perhaps due to its weaker basic strength (Yacob et al., 2009). Yacob et al. (2009) employed modified commercial nano-MgO to transesterify palm oil and achieved 51.3% biodiesel yield under optimal conditions (Yacob et al., 2009). Similarly, over 95% biodiesel yield was obtained from the transesterification of soybean oil via CaO and SrO catalysts, respectively, (Liu et al., 2007, 2008). Mesoporous materials including Al<sub>2</sub>O<sub>3</sub> was also used as the support to load various compounds to synthesize effective base catalysts (Arzamendi et al., 2007; Boz et al., 2009; Noiroj et al., 2009). Arzamendi et al. (2007) synthesized and tested NaOH-loaded Al<sub>2</sub>O<sub>3</sub> for transesterification of sunflower oil in which about 95% fractional conversion of oil was reported. Further, KOH and KF were also tested as the catalysts deposited on Al<sub>2</sub>O<sub>3</sub> by Noiroj et al. (2009) and Boz et al. (2009) and the reported highest biodiesel yield was 91.07% for palm oil transesterification and 97.77% for canola oil transesterification, respectively.

Nonetheless, these heterogeneous base catalysts are usually derived from commercial chemicals, and the preparation method sometimes consists of multiple complicated steps. As a result, those catalysts might become uneconomical, especially on a commercial scale. One possible way to address the problem is to synthesize

catalysts from agricultural wastes, lowering the production cost and alleviating environmental pressure simultaneously. Shells derived from natural sources tend to be a suitable choice due to their high accessibility and non-toxic features (Boro et al., 2012). A simple thermal conversion will convert natural shells into highly active CaO to catalyze transesterification. A modification step, like wet impregnation with other chemicals, could be combined with thermal conversion to improve the performance of shell-derived catalysts. Eggshell, crab shell, oyster shell, mussel shell and others have all been tested for transesterification (Boey et al., 2009; Hu et al., 2011; Jairam et al., 2012; Nakatani et al., 2009; Wei et al., 2009). Recently, eggshell was tested as a precursor for base catalyst to transesterify soybean oil to obtain a biodiesel yield of over 95% (Wei et al., 2009). Similarly, the crab shell and mussel shell were also chosen for base catalyst development by Boey et al. (2009) and Hu et al. (2011), respectively. Crab shell-derived catalyst led to a biodiesel purity of 98.8% during transesterifying palm olein, and mussel shell-derived catalyst provided a biodiesel yield over 90% by transesterifying Chinese tallow oil (Boey et al., 2009; Nakatani et al., 2009). Further, obtuse horn-derived calcium oxide catalyst was tested for transesterification of palm oil resulting in a fractional conversion of 86.7% despite low surface area (Lee et al., 2015). Similarly, Niju et al. (2016) observed that waste clam shell-derived calcium oxide catalyst was able to provide up to 94% FAME yields during transesterification of waste cooking oil (Niju et al., 2016). Chen et al. (2016) reported that abalone shells could be modified via ethanol treatment to enhance the catalytic activity, conversion, FAME yield, and catalyst reusability when applied to palm oil transesterification (Chen et al., 2016). Calcined waste shells from the egg, oyster, and clam shells were employed as base catalysts for transesterification of soybean oil by Risso et al. (2018).

The authors reported that the catalytic activity could be enhanced via hydration-dehydration-calcination cycles and the reaction followed an Eley-Rideal type mechanism. Recently, zinc-doped eggshell catalysts were investigated

by Borah et al. (2019) for transesterification of waste cooking oil and reported a 96.7% conversion (Borah et al., 2019). Their results indicate a promising situation where the shell-derived base catalysts could serve as the catalysts for biodiesel production.

In the southeastern United States, oyster shells are produced in huge quantities. The major component of oyster shell, similar to other natural shells, is calcium carbonate (Yoon et al., 2003). Calcium showed several functions in industrial application and also in human nutrition (Kaushik et al. 2015a; Kaushik et al. 2017, Kaushik et al. 2015b). Considering the chemistry of oyster shell, calcined oyster shells have been investigated for transesterification of oils. For example, Nakatani et al. (2009) used combusted oyster shells as the catalyst, and obtained a FAMES yield of 73.8% under optimal conditions (catalyst loadings 25% wt.) from their statistical model (Nakatani et al., 2009). Jairam et al. (2012) further enhanced calcined oyster shell by impregnating with KI, and reported an oil conversion of 85% using a molar ratio (MR) of oil to methanol of 1:6, catalyst loading (CL) of 3.5%, and reaction temperature of 60 °C (Jairam et al., 2012). Based on the surface chemistry of oyster shell, we hypothesize that oyster shell could be chemically modified to enhance the conversion of oil into FAME. Hence the goal of this research is to enhance the catalytic activity of oyster shell via chemical impregnation of NaOH. Specifically, the objectives were to investigate the effects of CL and methanol to oil ratio, and determine the durability of the catalyst.

## 2 Materials and methods

### 2.1 Catalyst preparation

Discarded oyster shells were collected from a local restaurant. The shells were washed with warm tap water to remove the dirt from the surface and dried at ambient temperature overnight. The washed shells were calcined at 500 °C for 2 h in a furnace (Paragon Industries) to remove the organic substances on the shell. Subsequently, the shells were crushed to a size of 1-2 mm and soaked in a 50%

NaOH solution at 90 °C for 5 h. After NaOH impregnation, shell particles were filtered and calcined at 1000 °C for 3 h under a nitrogen environment to obtain the final catalyst.

### 2.2 Catalyst characterization

The catalyst was characterized via an FTIR analyzer to study the surface functional groups. In addition, the basic strength of the catalyst was determined via various Hammett indicator tests using bromothymol blue ( $H = 7.2$ ), phenolphthalein ( $H = 9.3$ ), 2,4-dinitroaniline ( $H = 15.0$ ), and 4-nitroaniline ( $H = 18.4$ ) indicators. About 150 mg fresh catalyst was equilibrated with 2 mL of a Hammett indicator solution (diluted in methanol) for 2 h. The basic strength of the catalyst was determined as being stronger than the weakest indicator exhibiting a color change, but weaker than the strongest indicator exhibiting no color change. The basicity was measured using Hammett indicator-benzoic acid ( $0.01 \text{ mol L}^{-1}$  anhydrous methanol solution) titration method (Rahul et al., 2011).

### 2.3 Transesterification

Transesterification reactions were performed in 250 mL three-neck glass reactor in triplicates. A typical reaction consisted of 20 mL of soybean oil mixed with a predetermined amount of methanol and catalyst on a process-controlled hot plate (Isotemp, Fisher Scientific, Pittsburgh, PA). Temperature and stirring rate were set to desired values according to specific reaction condition requirements. In this research, the effects of the MR of methanol to oil and CL on FAME yields were studied. The reaction temperature and stirring rate were set to 62 °C and 800 rpm, respectively. After completion of the reaction, the reaction mixture was transferred to 50 mL plastic tubes and centrifuged at 5000 rpm for 8 min. The solid catalyst was removed, and the liquid mixture was washed with deionized water three times to remove excess methanol in the upper FAME phase. Washed samples were centrifuged again at 5000 rpm for 12 min, and 1 mL of the upper FAME phase was collected for further gas chromatographic analysis.

### 2.4 Gas chromatography analysis

The FAME concentration was determined using a gas chromatograph coupled with a mass spectrometric detector (Agilent 7890/5975C VLMSD) and equipped with an HP-Plot Q column. Ultra-high pure helium ( $3 \text{ L min}^{-1}$ ) was used as a carrier gas. The instrument was set to an inlet temperature  $250^\circ\text{C}$  while the oven temperature maintained at  $100^\circ\text{C}$  for 2 min and was increased to  $250^\circ\text{C}$  at a rate of  $15^\circ\text{C min}^{-1}$  and maintained at  $250^\circ\text{C}$ . Methyl laurate was used as an internal standard for quantitative analysis of FAME concentration. The ratio of FAME peak area to internal standard peak area was calculated for each sample. FAME yields were calculated using the equation below, as proposed by Liu et al. (2008) and Chung et al. (2009).

$$\text{Yield} = \frac{(\sum A) - A_{IS}}{A_{IS}} \times \frac{C_{IS} V}{m_{FAMES}} \times 100\% \approx \frac{(\sum A) - A_{IS}}{A_{IS}} \times \frac{C_{IS} V}{m_{oil}} \times 100\% = \frac{(\sum A) - A_{IS}}{A_{IS}} \times \frac{C_{IS} \times V}{\rho_{oil} \times \frac{1}{r} \times V} \times 100\% = \frac{(\sum A) - A_{IS}}{A_{IS}} \times \frac{C_{IS}}{C_{oil}} \times 100\% \quad (1)$$

where  $\sum A$  is the summation of peak areas of all methyl esters,  $A_{IS}$  is the peak area of the internal standard,  $C_{IS}$  is the concentration of the internal standard in the final diluted solution ( $\text{g mL}^{-1}$ ),  $V$  is the volume of the final diluted solution (mL),  $m_{FAMES}$  is the theoretical maximum mass of FAMES (g),  $m_{oil}$  is the mass of pure soybean oil of volume  $V$  (g),  $\rho_{oil}$  is the density of soybean oil ( $\text{g mL}^{-1}$ ),  $r$  is the dilution ratio of FAMES sample,  $C_{oil}$  is the corresponding concentration of soybean oil ( $\text{g mL}^{-1}$ ) in the final diluted solution if dilution ratio is  $r$ .

## 2.5 Comparison with calcined oyster shell

Calcined oyster shell (control) was chosen as the reference to evaluate the performance of the catalyst. Both catalysts were tested in transesterification reactions at  $62^\circ\text{C}$  (800 rpm) using a MR of 12 and a CL of 10%. Samples were drawn every hour and analyzed for FAMES yield.

## 2.6 Experimental design and statistical analysis

A crossed, two-factor randomized design was employed, with the levels of one factor, MR, set to 6, 12, 18, and 24

and the levels of the other factor, CL, set to 2%, 5%, 7%, and 10%. All 16 factorial combinations were performed at  $62^\circ\text{C}$  and 800 rpm. The FAME yields were determined and analyzed using SAS (SAS Institute Inc., Cary, USA). Factorial effects of MR and CL on FAME yields were investigated using analysis of variance along and Tukey's procedure to make pairwise comparisons of treatment combinations.

## 2.7 Reusability

Additional experiments were performed to determine the reusability of the catalyst. Based on the data obtained from the factorial experiments, conditions that provided the highest FAME yield were selected for catalyst reusability experiments. The catalyst was used for three successive runs. After each run, the FAME yields were recorded, and the recovered catalyst was applied to the subsequent run without any treatment. The FAME data were analyzed via a Tukey's HSD test.

# 3 Results and discussion

## 3.1 Catalyst characterization

The FTIR analysis of NaOH-impregnated calcined oyster shell displayed three significant major peaks at wavenumber  $1438 \text{ cm}^{-1}$ ,  $881 \text{ cm}^{-1}$ , and  $704 \text{ cm}^{-1}$ , compared with the calcined oyster shell (control), which had no significant peaks at these positions (Figure 1). These three peaks represented the asymmetric stretch, out-of-plane bend, and in-plane bend vibration modes attributed to  $\text{CO}_3^{2-}$  group (Boro et al., 2011). Because none of these peaks appeared for the calcined oyster shell (control), it implied that no  $\text{CO}_3^{2-}$  group existed in the oyster shell after calcination at  $1000^\circ\text{C}$ , suggesting that all  $\text{CaCO}_3$  had been decomposed into CaO. In comparison, NaOH-impregnated calcined oyster shell acquired these peaks, probably due to the pretreatment with NaOH solution.

The basic strength of the catalyst was found to be in the range of 9.3 – 15.0 (Table 1) with total basicity of 0.387

mmol g<sup>-1</sup> suggesting that the catalyst surface acquired basic characteristics after impregnation with NaOH and subsequent calcination.

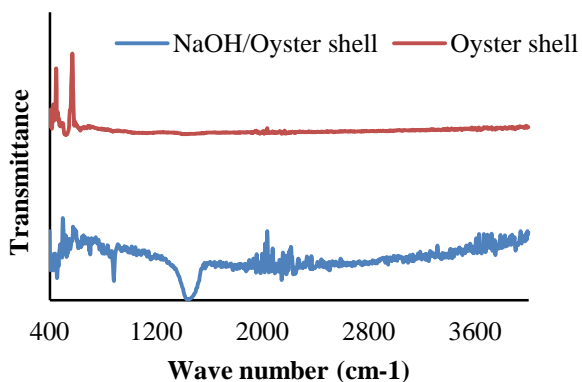


Figure 1 FTIR analysis of calcined oyster shell (control) and NaOH-impregnated calcined oyster shell.

**Table 1 Basicity distribution of the NaOH-impregnated calcined oyster shell catalyst**

Basic strength	Basicity (mmol g <sup>-1</sup> )
H <sub>-</sub> = 7.2 – 9.3	0.114
H <sub>-</sub> = 9.3 – 15.0	0.273
Total	0.387

### 3.2 Comparison with calcined oyster shell

Calcined oyster shell was applied for transesterification of soybean oil by Nakatani et al. (2009), in which a biodiesel yield 73.8% (MR of methanol to oil 6:1, CL 25%, reaction temperature 65 °C) was predicted after 5 h from their statistical model (Nakatani et al., 2009). In this work, the calcined oyster shell was used as the reference catalyst and for evaluating the efficacy of NaOH-impregnated calcined oyster shell. Both types of catalyst were tested under the same conditions (MR = 12, CL = 10%, reaction temperature = 62 °C, stirring rate = 800 rpm). Performances of both catalysts are shown in Figure 2. For the normal oyster shell, no FAMES formation was detected during the first hour. After 3 h reaction, the biodiesel yield reached to about 70%. In addition, biodiesel yield at 4 h seemed to reach a plateau, suggesting that the reaction was completed. However, for NaOH-impregnated oyster shell, the reaction seems to occur rapidly and seems to be complete around 1 h with a final biodiesel yield about 90%. Compared with normal oyster shell, NaOH-impregnated calcined oyster shell led to a faster reaction rate and higher biodiesel yield,

indicating that the NaOH solution pretreatment method had successfully improved the catalytic activity of oyster shell in soybean oil transesterification reaction.

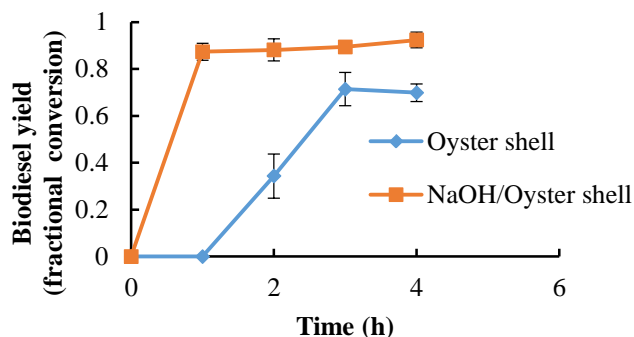


Figure 2 Comparison between calcined oyster shell (control) and NaOH-impregnated calcined oyster shell

Note: MR = 12, CL = 10%, temperature = 62 °C, stirring rate = 800 rpm.

### 3.3 Overall analysis of factorial design

The results obtained from factorial design experiments are summarized in Table 2 and 3. Both MR and CL showed a significant effect on FAME yields. In addition, a significant MR-CL interaction effect was observed, suggesting that the effect of either factor significantly depends on the specific level of the other. To interpret the effect of each factor, the simple effects of MR and CL were analyzed.

#### 3.4 Effect of methanol ratio (MR)

Figure 3 summarizes the effect of MR on the FAME yield. The overall analysis of the factorial experiment indicated a significant interaction effect between MR and CL, suggesting that the effect of MR depended on the specific level of the CL.

When CL was low (2%), increasing MR from 6 to 12 led to a significant increase in FAME yield from 29.3% to 55.4%. However, no significant increase in FAME yield was observed when MR was increased from 12 to 18 and 18 to 24. The increase in FAME yield from low MR (6) to high MR (12, 18, and 24) might be attributed to the higher availability of methanol to the active catalytic sites. Based on Le Chatelier's principle, an increase of reactant concentration shifted the equilibrium to the product side, thereby increasing FAMES concentration, which was also reported by Borah et al. (2019).

**Table 2 Results of the factorial design experiment**

Entry	MR	CL (%)	Yield (%)
1	12	5	86.4 ± 3.3
2	24	5	76.5 ± 2.8
3	6	5	71.4 ± 1.4
4	18	5	73.3 ± 1.6
5	12	10	93.9 ± 2.1
6	6	10	78.7 ± 1.8
7	18	10	86.2 ± 4.0
8	24	10	83.9 ± 4.5
9	12	2	55.4 ± 3.5
10	6	2	29.3 ± 1.3
11	18	2	71.6 ± 6.1
12	24	2	77.1 ± 4.0
13	12	7	88.9 ± 0.4
14	6	7	78.1 ± 4.3
15	18	7	90.2 ± 2.3
16	24	7	86.1 ± 3.1

Note: The reaction temperature, stirring rate and reaction time were set to 62°C, 800 rpm, 2 h, respectively.

**Table 3 Analysis of variance of FAME yields**

Sources	Sum of squares	Degrees of freedom	Mean of squares	F-value	P-value
MR	0.621	3	0.207	63.760	1.36 * 10 <sup>-13</sup>
CL	0.251	3	0.084	25.796	1.13 * 10 <sup>-8</sup>
MR * CL	0.282	9	0.031	9.654	6.08 * 10 <sup>-7</sup>
Residual	0.104	32	0.003		

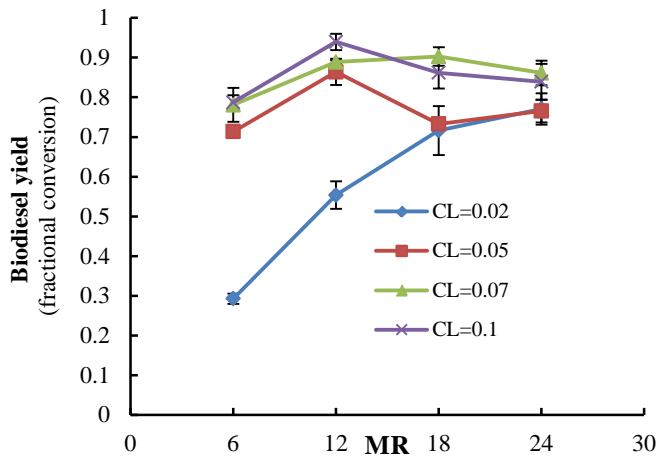


Figure 3 Effect of MR on FAMES yield at various CLs

Note: The reaction temperature, stirring rate and reaction time set to 62°C, 800 rpm, 2 h, respectively.

At higher CL, the effect of MR on increasing FAME yields became less significant. At CL of 5% and 10%, significantly different FAME yields existed between the highest and the lowest. At 7% CL, all four biodiesel yields for four MRs showed no difference between any two data

points. At 5%, 7%, and 10% CL, the highest biodiesel yield appeared to be at MR of 12. In addition, overall mean yield at MR of 6 was less than that at MR of 12, which might be attributed to the lower concentration methanol leading to an equilibrium shift to the reactant direction.

Interestingly, further increase of MR from 12 to 18 and 24 reduced the mean biodiesel yield as well, probably due to the relatively lower concentration of active catalytic sites resulting from an increase of methanol concentration as was also observed by Lee et al. (2015) and Chen et al. (2016), although other researchers observed no change in yields beyond an MR of 12 (Chen et al., 2016; Lee et al., 2015; Niju et al., 2016). Thus, MR of 12 appeared to be an optimal level of the catalyst when CL was in the range of 5% to 10%. Our results are somewhat similar to Rezaei et al. (2013), who investigated transesterification of soybean oil using calcined mussel shell as a catalyst. The authors reported an optimum yield of about 94% at an MR of 24 and 12% CL at 60 °C. Similar results were reported by Hu et al. (2011) who employed water-impregnated calcined freshwater mussel catalyst for transesterification of Chinese tallow oil, wherein the authors observed an optimum FAME yield of 97.5% using 5.3% CL and MR of 13.4.

**3.5 Effect of catalyst loading (CL)**

Figure 4 summarizes the effect of CL on FAMES yield at various MR levels. A significant increase of biodiesel yield was observed between 2% CL and 5% CL at MR of 6 and 12, suggesting that 5% CL provided more surface active sites than 2% CL.

Further increase of CL did not increase the yield, probably because the total number of the surface active sites of the catalyst was excessive for reactant adsorption, thus no improvement observed. At MR of 18 and 24, the increase of CL had no significant influence on the biodiesel yield. Tukey’s HSD indicated that there was no significant difference between any two biodiesel yields when MR reached 18 or 24.

Unlike the case for MR = 6 and 12, MR = 18 and 24 provided more methanol for transesterification, thus shifting equilibrium to the FAMES side, increasing the

biodiesel yield. Therefore, the low CL level (2% and 5%) could still achieve comparable yields when compared to those of CL = 7% and 10%. The effect of CL was weakened in the case of high MR, in which the effect of MR became dominant. Hence, the effect of CL at low MR level (6 and 12) was more significant than that at high MR level (18 and 24). From Figure 3, it was apparent that for any MR level in this experiment, the effect of CL was not significant once it exceeded 5%.

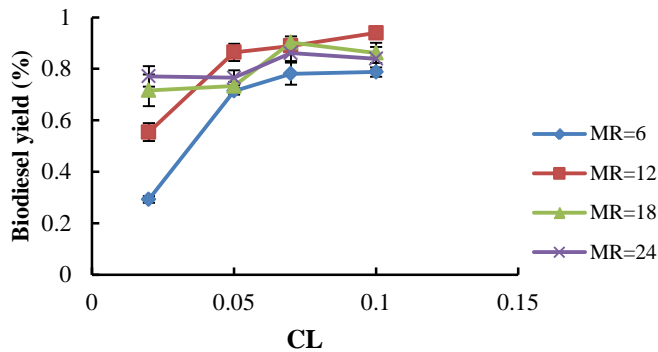


Figure 4 Effect of CL on FAMEs yield at various MRs

Note: Reaction temperature, stirring rate and reaction time were set to 62°C, 800 rpm, 2 h, respectively.

### 3.6 Reusability

Additional experiments were performed to verify the reusability of the catalyst. Because Tukey's HSD suggested no significant differences between several runs, experimental conditions based on the highest FAME yield (MR = 12, CL = 10%) were selected to investigate the repeatability of the catalyst. Three experiments were performed using the same catalyst at 62 °C (800 rpm). Results indicated that no significant differences in FAME yields were observed between three runs (Figure 5).

The FAME yields for all three runs were observed to be around 90%, suggesting that the catalyst was durable and possessed activity to catalyze transesterification for at least three times. Our results were somewhat similar to Hu et al. (2011) who investigated calcined freshwater mussel shell catalyst for transesterification of Chinese tallow oil (Hu et al., 2011). The authors reported that the catalyst maintained activity for up to 7 cycles. Similarly, Boey et al. (2011) reported that activated cockle shell catalyst was able to maintain activity for at least three times for transesterifying

palm oil (Boey et al., 2011). However, in the catalyst employed by Boey et al. (2011) required washing with methanol recalcination at 900 °C (2 h) for removal of adsorbed impurities. In our research, no visual impurities on the catalyst surface were observed (Boey et al., 2011). Similar results were reported by Wei et al. (2009) and Chen et al. (2016) who investigated calcined eggshell for transesterification of soybean oil and palm oils, respectively (Chen et al., 2016; Wei et al., 2009). The authors reported no loss of activity even after the catalyst was reused several times and simple calcination was expected to reactivate the catalyst. Some authors, however, observed a decrease in FAME yields when the catalyst was reused. Obtuse horn-derived calcium oxide catalysts exhibited decreased activities after third reuse (Lee et al., 2015). The FAME yields decreased from 90% after first reuse to about 70% after third reuse and to about 30% after fourth reuse, which was attributed to pore blockage and loss of active sites via leaching. Similarly, Borah et al. (2019) reported consistent decrease in FAME yields with each reuse that dropped from 95% to 70% after five successive cycles due to loss of active sites (zinc) from the CaO surface (Borah et al., 2019). However, in our research, NaOH-impregnated calcined oyster shell catalyst maintained consistent activity and has the potential to serve as a solid base catalyst for transesterification of oils into FAMEs.

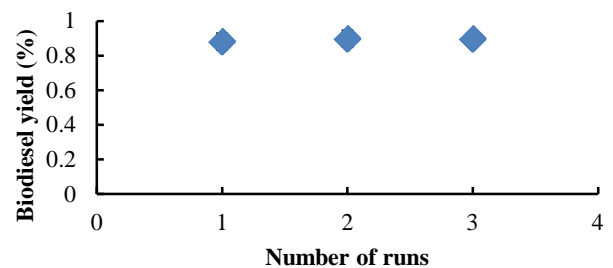


Figure 5 Reusability test of NaOH-impregnated calcined oyster shell

Reaction conditions: MR = 12, CL = 10%, temperature = 62°C, stirring rate = 800 rpm, reaction time=2 h

## 4 Conclusions

A highly active solid base catalyst was synthesized by wet impregnation of NaOH on an oyster shell, followed by

calcination. The basic strength of this catalyst was measured to be in the range of  $9.3 < H_- < 15.0$ . This catalyst was found to be highly active for soybean oil transesterification, with FAME yield exceeding 93% under the optimal conditions of MR = 12, CL = 10%, a reaction temperature of 62 °C, and a stirring rate 800 rpm. The catalyst was employed in soybean oil transesterification for at least three runs without any significant decrease in FAME yield, suggesting that it is suitable for biodiesel production.

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