



## Efficient solid base derived from eggshell for heterogeneous biodiesel production

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In this work, eggshell waste was investigated in a triglyceride transesterification with a view to determine its pretreatment and viability as a solid base for the biodiesel production, which can reduce the cost of biodiesel to make it competitive with petroleum diesel. Eggshell waste was treated with acid and the produced powder was calcined before the use of solid base catalyst. The physical properties of the catalyst were characterized using the Fourier Transform-infrared (FT-IR) spectroscopy, CO<sub>2</sub>-Temperature Programmed Desorption (TPD), X-ray Diffraction (XRD), and Scanning Electron Microscopy (SEM), and the biodiesel conversion was determined by the Gas Chromatography (GC). It was found that the acid type used in pretreatment has a great effect on the catalytic performance of obtained CaO, and 5 wt% CaO derived from HCl treated eggshell waste is superior to the commercial CaO. The maximum percentage yield of biodiesel by using derived CaO is 99.2% under optimum conditions of 10:1 methanol to oil ratio after 4 h at 65°C, while for commercial CaO, 74.9% yield of biodiesel with 10:1 methanol to oil ratio after 4 h.

**Keywords:** Biodiesel, CaO catalyst, Eggshell waste, Pretreatment, Transesterification

With increasing demand for energy and more attention about the environment, it is urgent to seek for an alternative fuel which can supplement or replace diesel<sup>1,2</sup>. Biodiesel is an alternative fuel for diesel engines with renewability, biodegradability, low emission profiles without sulfur, high flashpoint and excellent lubricity<sup>3</sup>. The most common way to prepare biodiesel is a chemically reaction of triglyceride with short-chain alcohol, such as methanol<sup>4</sup>. The transesterification can be catalyzed efficiently under basic react condition. In order to avoid the problem for catalyst separation, various heterogeneous alkali catalysts have been widely used in biodiesel production<sup>5,7</sup>. Recently, alkaline metal compounds have been regarded as good heterogeneous catalysts for the transesterification of triglycerides<sup>8</sup>. Among the different basic oxides, CaO exhibited good catalytic activity in transesterification with 98% conversion within 8 h<sup>9</sup>. The basicity of CaO, as well as the catalytic activities, for transesterification was promoted by loading alkali metal to CaO<sup>10</sup>. Some interesting results were obtained in the transesterification of

vegetable oil and methanol in the presence of bulk CaO, in particular nano CaO prepared by different methods<sup>11,12</sup>. Tang *et al.* developed a novel KCl/CaO nanocatalyst by impregnation method, and it showed excellent activity to convert Chinese tallow seed oil to biodiesel<sup>13</sup>. However, the reusability is one of the serious problem associated with the heterogeneous basic catalysis. Tang *et al.* produced biodiesel using nanocrystalline CaO under room temperature<sup>14</sup>, and the results showed that the first three cycles provided >99% conversion, decreasing conversions were obtained in the fourth and fifth cycles, respectively. Therefore, it is a great challenge to develop a solid base catalyst for transesterification process with stable activity. Recently, the utilization of cost effective and environmental friendly waste materials has gained a promising scope for biodiesel production<sup>15,16</sup>. Boro has demonstrated the excellent properties of calcium oxides derived from eggshell in transesterification reaction<sup>17</sup>. Due to the texture of eggshell is complex by containing three layers, the treatment of eggshell should be important to obtain porous properties eggshell based CaO.

In this present work, an efficient CaO with good stability was prepared from cheap and easily available

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eggshells and was thoroughly investigated for its characteristics and catalytic activity towards transesterification of vegetable oil for biodiesel production. All reaction conditions were optimized, and the effect of treatment conditions of eggshell including the types of acids on the catalytic performances of obtained CaO has been investigated in detail.

## Materials and Methods

### Materials

Rapeseed oil was purchased from a coal market (Xi'an, China). Before the reaction, the oil was treated by sodium hydroxide and bentonite in which the acid value lowers than 1 mg KOH/g and water concentration below 1 mg/mL. All the chemicals were of an analytical reagent grade and were obtained from Sinopharm Chemical Regents Co., Ltd. (Beijing, China). Waste egg shells were collected from the Walmart Market, Xi'an, China.

### Catalysts preparation

The egg shells were washed thoroughly in tap water to remove any unwanted material adhered on its surface firstly, and rinsed with amount of acid. The treated egg shells were then dried in hot air oven at 105°C overnight. The dried egg shells were grind into powder and calcined in a muffle furnace under static air condition at settled temperature for 2.5 h to transform the calcium species in the shell into CaO particle.

### Catalytic testing

The catalytic activities for the transesterification of rapeseed oil with methanol were measured by typical procedure<sup>18</sup>. A given amount of catalyst and methanol was placed in a three necked round bottomed flask equipped with a reflux condenser and a thermometer. Then, the rapeseed oil was introduced into the mixture and heated at a certain temperature for a certain time. After the reaction completed, the catalyst was separated by filtration and the excess methanol was distilled off under vacuum. The products were analyzed by the GC (HP-6890) using inner standard. The yield was defined as a ratio of the weight of fatty acid methyl esters, determined by GC, to the weight of fatty acid methyl esters that the oil used in the reaction, assuming only traces of esters transferred to the polar phase, and only the extraction of methanol and glycerin takes place as suggested by López<sup>19</sup>.

### Catalyst stability

The lifetime of the commercial CaO and modified CaO was evaluated by repeating transesterification

several times with used catalysts under the optimum reaction condition. Used catalysts were separated from the previous reaction mixture by centrifugation, washed with hexane, and then dried at 60°C. The product was subjected to GC analysis for the FAME determination, as described earlier<sup>20</sup>.

### Catalyst characterization

Thermogravimetric (TG) analysis was performed under air flow on a Q600 SDT thermal analysis machine (TA Instruments, USA) with a heating rate of 10°C/min up to 800°C. The Fourier transform-infrared (FT-IR) spectra were used to identify the surface group over the catalyst. X-ray diffraction (XRD) patterns were recorded on a D/Max-3C X-ray powder diffractometer (Rigaku Co., Japan), using a Cu-K  $\alpha$  source fitted with an Inel CPS 120 hemispherical detector. Scanning electron microscope (SEM) photographs were taken by Quanta 200 scanning electron microscope equipped with an energy dispersive spectrometer (Philips-FEI Co., the Netherlands). BET analysis was conducted using an ASAP 2020 surface area analyzer (Micromeritics). The basicity studies of the catalysts were conducted with CO<sub>2</sub>-TPD in a Chem BET-3000 (Quanta Chrome, USA) instrument.

## Results and discussion

### Characterizations of the catalysts

Treated egg shells and commercial CaO without calcination were investigated by thermogravimetric analysis as shown in (Fig. 1). Based on Figure 1, the steps TG curve of commercial CaO in the temperature range from 400-500°C due to the loss of H<sub>2</sub>O from hydrated, which indicates that the poisoning effect of H<sub>2</sub>O adsorption is very obvious<sup>21</sup>. However, the

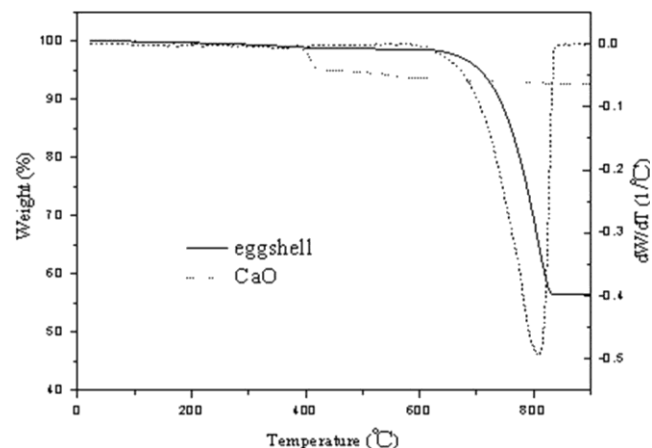


Fig. 1 — The TG curves of commercial CaO and treated egg shells

desorption temperature located at 800°C corresponds to decomposition of  $\text{CaCO}_3$  due to the carbonation of egg shell, which is enhanced rapidly even amount of acid introduced to the treatment process. Furthermore, from the percentage of weight loss corresponding to the decomposition of  $\text{Ca(OH)}_2$  in both samples, 2.305% for commercial CaO and 0.451 % for egg shells, it can be concluded that the amount of  $\text{Ca(OH)}_2$  formed during the calcination procedure is relatively less.

Figure 2 shows the IR spectra of CaO derived from egg shells after calcined at different temperatures. For all the samples, the spectra display bands at  $867\text{ cm}^{-1}$  and  $1477\text{ cm}^{-1}$ , which correspond to vibration modes of mono and bidentate carbonates. The bands at  $1621\text{ cm}^{-1}$  can be assigned to isolated OH groups present at the surface of the CaO solid<sup>22</sup>. Some hydroxyls bands, those at  $3460\text{ cm}^{-1}$  and  $3572\text{ cm}^{-1}$ , can be assigned to OH groups of  $\text{Ca(OH)}_2$ <sup>23</sup>. It is also evidenced from the characteristic absorb of C=O between  $2000\text{ cm}^{-1}$  and  $1500\text{ cm}^{-1}$  that the presence of calcium carbonate formed in the catalyst<sup>24</sup>, as evidenced by the two characteristic broad diffraction lines of CaO in the diffraction pattern (Fig. 3). Apparently, their intensity gives less value, when calcination temperature was settled at 800°C, suggesting the easier decomposition of carbonate over solid surface.

Figure 3 shows the XRD pattern of the uncalcined and calcined catalysts. For the uncalcined sample and the sample calcined at 700°C, minor reflections at 17.9, 28.6, 34.1, 46.9 and 50.7 attribute to  $\text{Ca(OH)}_2$  phases, indicating the hydration of egg shell. As suggested by TG result (Fig. 1), for eggshells, the

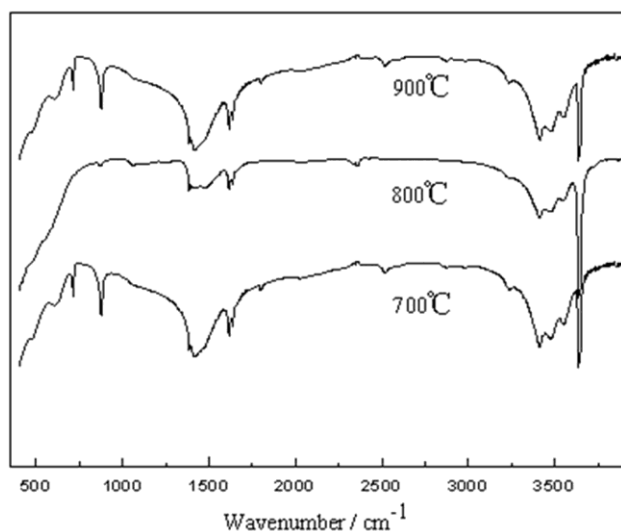


Fig. 2 — FT-IR of the egg shells calcined at different temperature

peak at 29.2 and 38.9 assigned to the reflection of  $\text{CaCO}_3$  means it still exists even calcination temperature raised to 700°C. During calcination above 800°C, a series of reflection at 32.1, 37.3 and 53.9 is consistent with X-ray diffractograms, which indicates that most  $\text{CaCO}_3$  in eggshell decomposed whereas CaO phase is the mainly part in the calcined eggshell<sup>25</sup>. Comparing the main peak area, it can be seen that the diffraction peaks corresponding to the CaO phases of eggshell calcined at 800°C are slightly less intense than those at 900°C, suggesting its higher dispersion by a loss of crystallinity as suggested by Paula<sup>26</sup>.

The BET surface area, total pore volume and pore diameter of eggshells calcined at different temperature were measured and summarized in (Table 1). According to the results, it can be found that the eggshell calcined at 800°C processes a higher surface area and larger pores, which is favorable for the use in the liquid-solid heterogeneous phase reactions due to the large reaction area in stirred reactor. This gradual increase of surface area with calcination temperature should be attributed to more exfoliate of CaO to form sheeted morphology at relatively high calcination temperature as confirmed

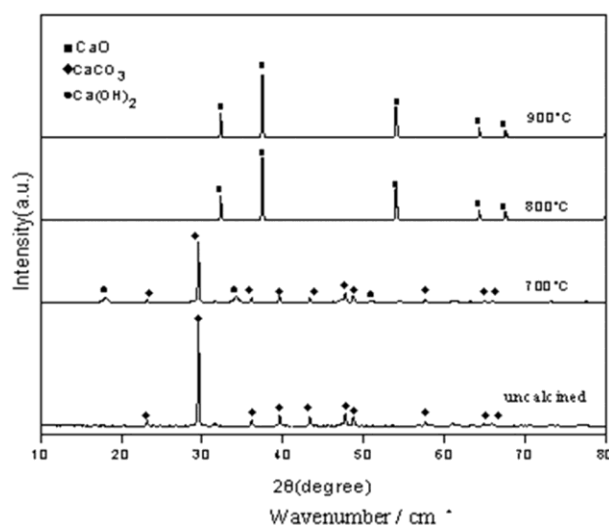


Fig. 3 — X-ray diffraction patterns of calcined and uncalcined catalysts

Table 1 — BET surface and pore properties of eggshell calcined at different temperature

Calcium source	BET surface area ( $\text{m}^2/\text{g}$ )	Pore volume ( $\text{cm}^3/\text{g}$ )	Pore size (nm)
700°C	2.8732	0.0052	6.03877
800°C	8.8730	0.0192	8.66540
900°C	6.9388	0.0135	7.80599

by SEM results. However, in the case of eggshell calcined at 900°C, the decrease of surface area, pore volume and pore size may be due to the sintering of catalyst and large particle formed as suggested by relatively high diffraction intensity of eggshell calcined at 900°C shown in (Fig. 3).

The SEM micrographs of eggshells calcined at different temperature were shown in (Fig. 4). Great difference can be found between the two samples. It can be seen that the surface of eggshell particle calcined at 700°C is built of aggregates similar with the results of Hu *et al.*<sup>27</sup>. As increase the calcination temperature, eggshell presents a regular micro morphology of rod like particles, which could be associated with its higher catalytic actives.

CO<sub>2</sub> temperature programmed desorption was conducted to determine the basic sites and properties in each catalyst. As suggested by Ramos *et al.*<sup>28</sup>, the CO<sub>2</sub> desorption peak over solid base is affected by the interaction of CO<sub>2</sub> with the occluded oxide species, which is associated with the anionic electronegativity so as to its basicity. The CO<sub>2</sub>-TPD profiles of the eggshells calcined at different temperature were shown in (Fig. 5). The TPD result of all samples shows a broad peak above 500°C. In the case of 800°C calcined eggshell, the TPD profile shows one strong and sharp peaks above 700°C, which is the characteristic of CO<sub>2</sub> desorption from strong basic sites. Furthermore, the total basicity of the derived CaO catalysts was evaluated by the TPD-CO<sub>2</sub> profiles and displayed in (Table 2). Derived CaO calcined at 700°C showed a desorption peak in the temperature range of 600-620°C, with 0.832 mmol/g of CO<sub>2</sub> desorbed, indicating the number of basic site in it is small, hence this catalyst is not very active in transesterification process. On the other hand, a desorption peak with larger amount of CO<sub>2</sub> desorbed (8.342 mmol/g) was observed from eggshell based

CaO calcined at 800°C over the temperature of 700°C. As we now known, the basic strength of the alkaline metal oxides has a deep relationship with its catalytic activity for transesterification. Furthermore, the number of basic sites over catalyst surface was increased suggested by the relatively larger CO<sub>2</sub>-TPD area of eggshell calcined at 800°C as shown in (Fig. 5), which leads to its high catalytic activity in the transesterification. From above results, it is important to find the effect of calcination temperature on the surface basicity of eggshell, which is the most important factor for the high reaction rate of the catalyst.

#### Catalytic activities test

##### Influence of acid treatment

In order to enhance the catalytic activity, a very weak acid solution was used to remove the dense cuticle layer of quail eggshells. In our work, it is first time that kinds of acids were screened as treatment agent for eggshell, and then the corresponding CaO was tested for the transesterification of rapeseed oil with methanol to produce biodiesel at react temperature of 65°C with molar ratio of methanol

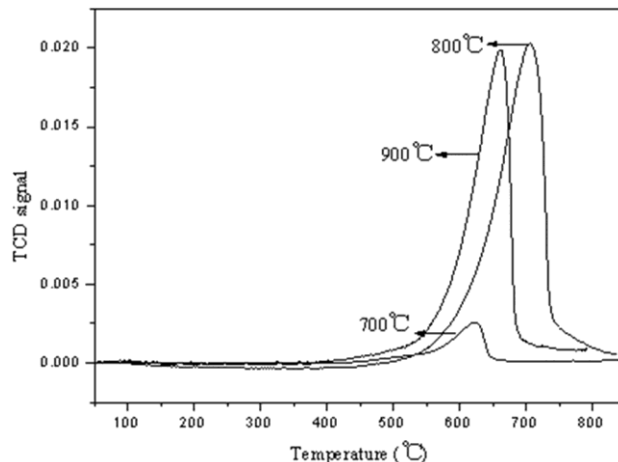


Fig. 5 — CO<sub>2</sub>-TPD of eggshell calcined at different temperature

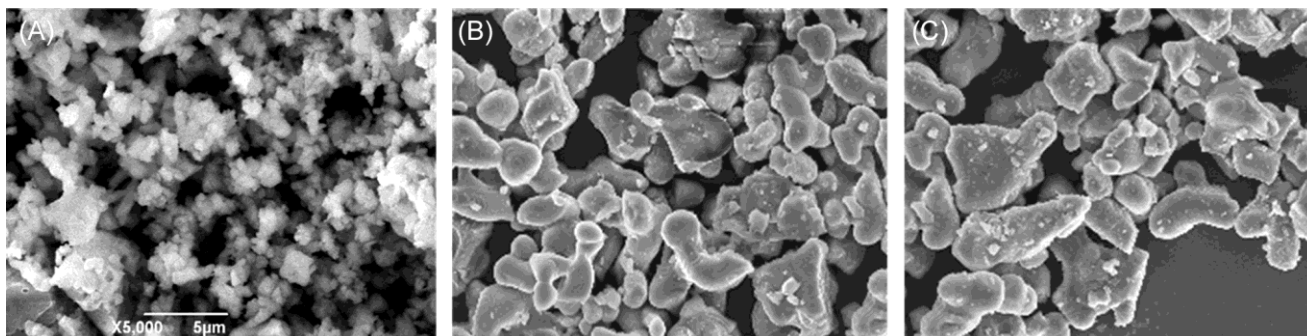


Fig. 4 — Scanning electron microscope pictures of eggshell calcined at (A) 700°C; (B) 800°C; and (C) 900°C

Table 2 — CO<sub>2</sub>-TPD results of eggshell based CaO calcined at different temperatures

Calcium temperature	Total basicity (mmol/g)	Desorption peaks (area%)
700°C	0.832	0.1935
800°C	8.342	1.9458
900°C	4.453	1.0355

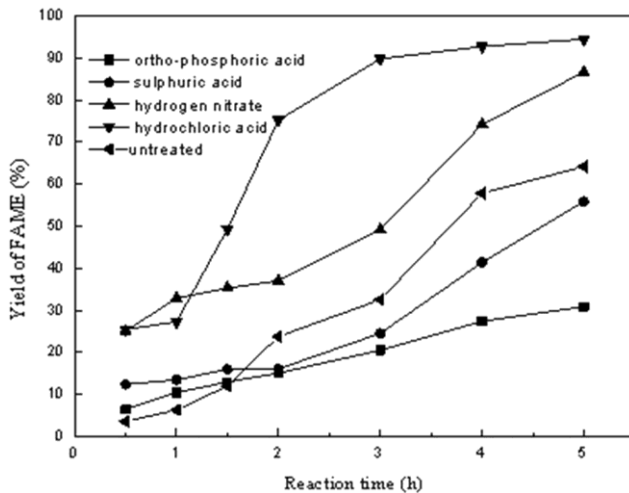


Fig. 6 — FAME yield over eggshell treated by different acid

to oil at 12:1 using 3 wt% catalyst<sup>29</sup>. The results of (Fig. 6) indicate that the yield of FAME increases over eggshell based CaO calcined under 800°C after HNO<sub>3</sub> and HCl treated, the yield reaches the maximum value when 0.005 M HCl was used. The mainly reason should be contributed to the palisade layer of eggshells which has many large pores, and HCl can eliminate the inactive layer and expose more palisade layer so as to accelerate the diffusion of large oil molecules in the porous materials<sup>30</sup>.

#### Influence of acid concentration

To remove the dense cuticle layer over eggshell completely, in our work, concentration of HCl was investigated from 0.005-0.015 M. From the result as shown in (Fig. 7A), it can be found that the yield of FAME decreases trendly with concentration of treated acid, and the eggshell pretreated by 0.005 M obtained the highest FAME yield of 98.2% at react temperature of 65°C with molar ratio of methanol to oil at 12:1 using 3 wt% acid-treated eggshell based CaO calcined under 800°C as catalyst<sup>29</sup>. The results of (Fig. 7A) indicate that 0.005 M HCl was enough for eggshell to remove its dense cuticle layer and enhanced its catalytic activity by increasing the fraction of the porous palisade layer.

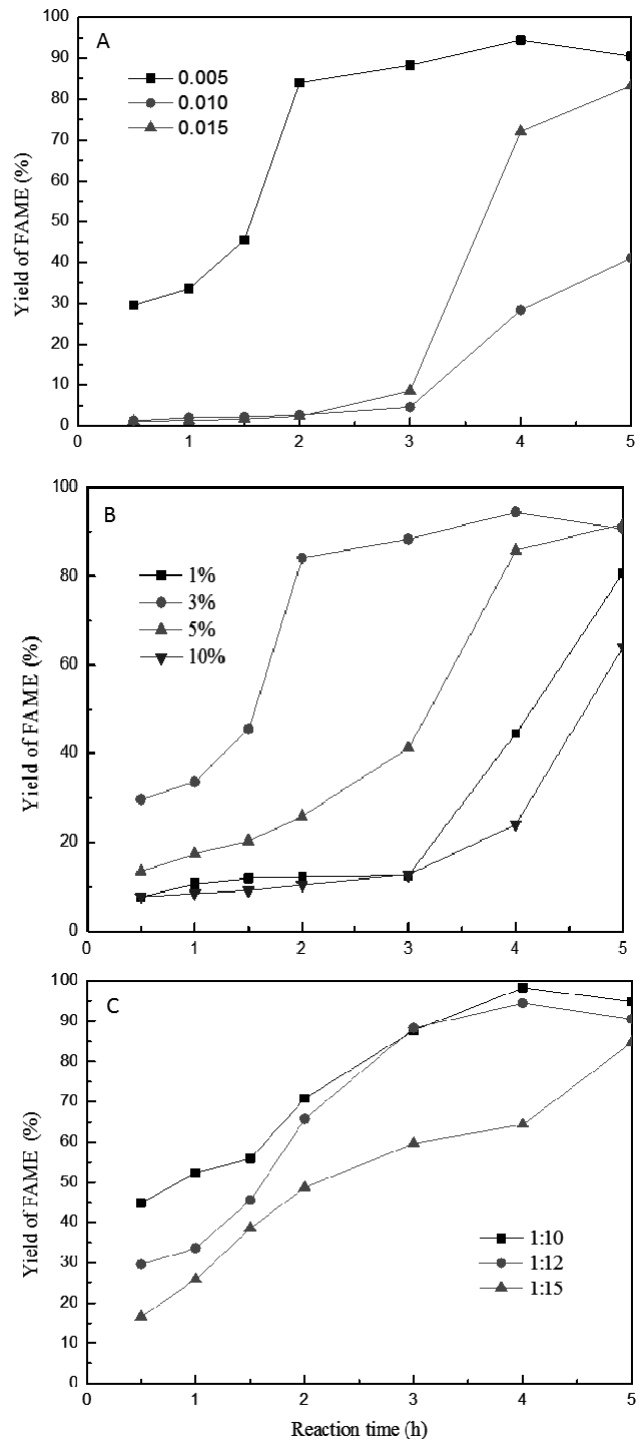


Fig. 7 — Effect of (A) Concentration of HCl; (B) Catalyst concentration; and (C) Methanol to oil ratio on FAME yield

#### Influence of catalyst concentration

The amount of catalyst is an important factor to the yield of the biodiesel production. The effect of eggshell based CaO calcined under 800°C concentrations on the transesterification was investigated with catalyst

concentration varying from 1 wt% to 15 wt% (weight to oil) at 65°C with methanol/oil molar ratio of 12:1. Figure 7B shows the yields of FAME ester using different catalyst concentration. Low concentration of catalyst (<3 wt%) is insufficient to catalyze the reaction for completion<sup>31</sup> and the maximum yield of FAME was only 75.2% during the reaction process. Increasing the amount of catalyst, the results of FAME yield changed greatly and the highest FAME yield (98.2%) was achieved for catalyst concentration of 5 wt%. No further enhancement of FAME yield was gained as excess catalysts were introduced because of the formation of soap in presence of high amount of catalysts.

#### *Influence of methanol/oil ratio*

As we now known, 3 mole of alcohol are required for each mole of triglyceride stoichiometrically according to the chemical reaction equation between them, in practice an excess of alcohol is used in biodiesel production to ensure that the oils or fats converted completely to esters in a short time<sup>32</sup>. In present work, the transesterification of rapeseed oil was carried out at 10:1, 12:1 and 15:1 molar ratios of methanol to oil with eggshell based CaO calcined under 800°C concentration fixed at 5 wt%. The reaction temperature was also set at the boiling point of methanol. As shown in Figure 7C, the yield of FAME was greatly influenced by the quantity of methanol when the molar ratio was increased from 10:1 to 12:1; the yield of FAME increased from 90.3% to 99.2% within 4 h. Further increase of methanol amount has negative effect on the FAME yield.

#### **Repeated experimental of the eggshell**

Generally, reusability is very important to evaluate the economic viability of a catalyst for biodiesel production. To evaluate the reusability of eggshell based CaO, the FAME yield of eggshell based CaO calcined under 800°C was examined for 5 cycles with 5% catalyst, a methanol to oil ratio of 12:1, a reaction temperature of 65°C and a reaction time of 4 h, and the results were shown in (Fig. 8). From the result, it can be found that the yields after each cycle reached to above 90%, indicating its promising potential in industrial application. However under these conditions, commercial CaO exhibited poor catalytic activity and produced a low FAME yield of 82.9% at the second time. It can be concluded the relative higher stability of CaO particle derived from eggshell.

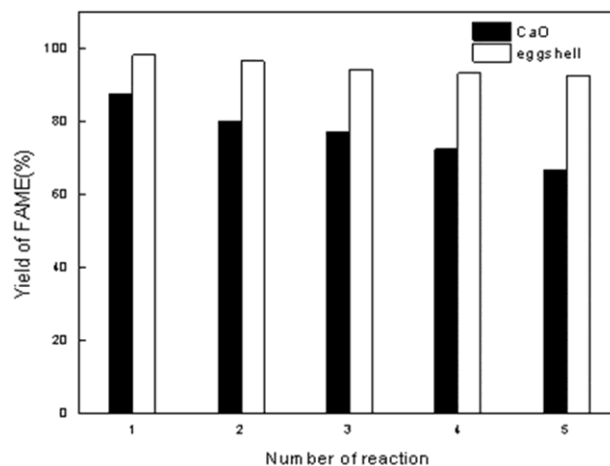


Fig. 8 — FAME yield over reused eggshell

The good reusability of eggshell based CaO should be contributed to its good thermal behavior as suggested before which ensure its same composition and surface properties after re-calcination.

#### **Conclusion**

An efficient solid base catalyst with high thermal stability derived from waste materials was obtained based on acid-treated eggshell. It was found that the type of acid has great effect on the surface properties of obtained eggshell based CaO and the HCl treated eggshell showed the highest catalytic performance in the transesterification of vegetable oil with methanol contributed to its large pores and a large amount of strong basic sites. Thus, 99.2% yield of biodiesel by using HCl treated eggshell based CaO under optimum conditions of 10:1 methanol to oil ratio after 4 h at 65°C was obtained, which is an exceptional catalytic activity comparable to that of homogeneous catalyst. The results from the present work have potential industrial applications for the low cost and easily obtainable materials in biodiesel production.

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#### **Conflict of interest**

All authors declare no conflict of interest.

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