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# EFFECT OF PRE-HEATING TIME AND REACTION TIME ON BIODIESEL YIELD

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## ABSTRACT

*Worldwide petroleum reserves are decreasing rapidly; therefore, looking for sustainable and renewable energy is currently one of the targets of scientists. Biodiesel which can satisfy these requirements is synthesized by the transesterification of plant/animal oil with alcohols, typically methanol, catalyzed by acid or base. Calcium oxide (CaO) derived from the eggshell shell can be used as a catalyst in the transesterification of oil with methanol because of its low solubility in methanol, high alkalinity and reusability which conform to environmentally-friendly process. In this research, induction period, rapid reaction period and equilibrium period were observed in the rate-time curve when CaO was used as a catalyst for the transesterification of soybean oil with methanol. CaO was preheated in methanol for 15 minutes before soybean oil was added and reaction started. It was found that pre-heating of CaO could significantly shorten the reaction time and resulted in 92.53% of the yield of fatty acid methyl esters. Moreover, this study contributes new information when CaO is used as the catalyst for biodiesel production.*

***Keywords:*** *biodiesel; transesterification; calcium oxide; soybean oil; calcium methoxide.*

## 1. INTRODUCTION

Nowadays, the world is facing many problems such as the increase of population growth, energy crisis and environmental pollution. Looking for potential energy sources is a target of scientists in order to ensure energy demand. Biodiesel is recently being used as an alternative, biodegradable and sustainable energy [1, 2, 3]. Biodiesel can be produced from different kinds of feedstock such as soybean oil, rapeseed oil, palm oil and sunflower oil [4, 5]. Biodiesel from soybean oil is of great importance because according to the report of UFOP, worldwide soybean oil production was about 348 million tons. Biodiesel produced from soybean oil ranked second (about 27%) in the total amount of worldwide biodiesel production in 2016 [6].

Biodiesel is mostly synthesized by transesterification of plant oil/animal fat with methanol using the acid/base as a catalyst [7]. There are many homogeneous catalysts which can be applied for transesterification such as NaOH, KOH, $H_2SO_4$, HCl and $CH_3ONa$ [8, 9]. Although using homogeneous catalysts, high product yield can be obtained in short reaction time; there are still some obstacles such as the recovery of catalysts, an expensive separation process with a high amount of wastewater produced and unwanted by-products soap due to high water and free fatty acids content of raw materials [8]. In order to overcome the difficulties of using homogeneous catalysts, heterogeneous catalysts were employed [2, 3, 7, 8, 9]. Among alkaline and earth alkaline metals, calcium oxide (CaO) has drawn attention for its best activity-price relation, low solubility in methanol, abundant in nature and environmentally friendly [7]. It can be prepared from different materials such as limestone, chicken eggshell, scallop shell and oyster shell with calcium carbonate as their main constituent [10].

In this study, CaO was used as the catalyst in producing biodiesel from soybean oil. The target of this study was to investigate the effect of preheating of CaO catalyst on transesterification reaction.

## 2. MATERIALS AND METHODS

### 2.1 Materials

Refined soybean oil was bought from Taiwan Sugar Corporation, Taiwan. The chemicals including methanol, n-hexane, ethyl acetate, benzoic acid, bromothymol blue (BTB), sodium hydroxide, sodium chloride and potassium hydroxide were obtained from commercial sources such as Sigma-Aldrich (USA), Fisher Scientific (UK) and Acros (Belgium). All of these chemicals were directly used without any further purification. Standards of FFAs, acylglycerides and FAME (fatty acid methyl ester) were purchased from Supelco (Bellefonte, PA).

### 2.2 Preparation of CaO

Eggshells were collected from a canteen in the campus of National Taiwan University of Science and Technology, Taipei, Taiwan. Impurities such as inner membrane were removed, the eggshells were washed with DI water and dried in an oven at 60 °C; then ground and sieved to obtain particle sizes from 40 to 100 mesh. CaO was obtained by calcining eggshell particles in a muffle furnace at 900 °C for 2 hours and carefully stored in a desiccator.

### 2.3 Characterization of CaO

### Basicity of catalyst

Briefly, 0.1 g of CaO was put into an Erlenmeyer flask with 1 g of benzoic acid and 50 mL methanol and 1 mL BTB indicator dissolved in methanol was added into the mixture. The reaction was stirred at $30^{o}$C for 4 hours. The blank sample was also prepared without the presence of CaO. After the reaction, the sample was titrated using standardized KOH until the equivalence point was reached. The basicity was calculated by the following equation.

$$\text{Basicity of catalyst}\left(\frac{\text{mmol OH}^-}{\text{g catalyst}}\right) = \frac{V_{\text{KOH of blank}} - V_{\text{KOH of titrant}}}{\text{weight of CaO}} \times N_{\text{KOH}} \quad (1)$$

Where $V_{\text{KOH of blank}}$ (mL) is the volume of KOH without CaO; $V_{\text{KOH of titrant}}$ (mL) is the volume of KOH reacted; Weight of CaO (g) is the amount of CaO used and $N_{\text{KOH}}$ (mmol/ml) is the molar of KOH

### FTIR analysis

A Bio-Rad FTS-3500 spectroscopy was used to determine the CaO and Ca-M. The sample was mixed with potassium bromide (KBr), pressed into a thin cake and tested by a monochromatized light beam. The spectrum was obtained in the transmission mode in 400-4000 $\text{cm}^{-1}$ at a resolution of 4 $\text{cm}^{-1}$ with 40 scans per sample.

### 2.4 Oil characterization

### Saponification value (SV)

One gram of oil was put in a flat bottom flask with 50 mL of 0.15 N alcoholic KOH. The flask was connected with a condenser and immersed in a water bath at 90 °C under stirring for 1 hour. After saponification, the sample was analyzed by acid-base titration. The volume of the standardized HCl solution used for sample was recorded. SV and average molecular weight of the oil sample were calculated by using the following equations:

$$\text{SV}\left(\frac{\text{mg KOH}}{\text{g oil}}\right) = \frac{\left[V_{\text{HCl of blank}} - V_{\text{HCl of sample}}\right] \times N_{\text{HCl}} \times 56.1}{\text{weight of oil}} \quad (2)$$

$$\text{MW}_{\text{AV}} = \frac{1000 \times 56.1 \times 3}{\text{SV}\left(\frac{\text{mg KOH}}{\text{g oil}}\right)} \quad (3)$$

Where $V_{\text{HCl of blank}}$ is the volume of HCl without oil; $V_{\text{HCl of sample}}$ is the volume of HCl reacted; $N_{\text{HCl}}$ (N) is the molar of HCl and Weight of oil (g) is the amount of oil used

### Acid value (AV)

One-half gram of sample and 50 mL of neutralized ethanol were put into a flask. The mixture of ethanol and oil was heated and kept at 60 $^oC$ for 5 minutes. Five drops of PP solution were then added. The sample was titrated by standardized KOH until its equivalence point. AV was calculated using the equation.

$$\mathrm{AV}\left(\frac{\mathrm{mg\ KOH}}{\mathrm{g\ oil}}\right)=\frac{\mathrm{V_{KOH}}\times \mathrm{N_{KOH}}\times 56.1}{\mathrm{weight\ of\ sample}} \quad (4)$$

### 2.5 Transesterification of oil

Methanol and catalyst were mixed in a two-necked flat bottle flask with a magnetic stirrer. The reaction was carried out in a water bath with a condenser to avoid solvent evaporation. After reaching 60°C, preheated methanol and CaO were stirred at 300 rpm for the desired time. Oil was separately treated by heating to 60$^o$C, then added into the mixture to start the reaction. After the reaction, the flask was cooled down to room temperature. Solid was collected by filtration and the product was transferred to a separatory funnel, then 50 mL of n-hexane and 20 mL of 5 wt.% NaCl were added to separate the oil phase and the aqueous phase. The upper phase containing methyl esters was withdrawn and recovered by removing n-hexane using a rotary evaporator. Crude biodiesel was weighed and analyzed by gas chromatography (GC). Each reaction was repeated at least twice.

### 2.6 GC analysis

A ZB-5HT column (15 m length, 0.32 mm i.d., 0.1 mm film thickness; Zebron, Phenomenex, Torrence, CA) was used for analyzing biodiesel samples in a GC 2010 with AOC 20i auto-injector. Briefly, 25 mg of sample was dissolved in ethyl acetate (1 mL) and homogenized using a vortex mixer. The diluted sample was filtered by a syringe filter with 0.2 μm PVDF membrane which had anhydrous $MgSO_4$.

$N_2$ was used as the carrier gas at a flow rate of 1.4 mL/minute. The analysis time was 29 minutes. The temperature of split injector and flame ionization detector were fixed at 370$^o$C while temperature profile was set from 80$^o$C to 365$^o$C with an increasing rate of 15$^o$C/minute. After this point, over temperature was fixed at 265$^o$C until the program was finished. An amount of 1.5 µL filtered sample was injected into GC. GC solution version 2.3 was used for data analysis.

## 3. RESULTS AND DISCUSSION

The molecular weight of oil as determined by saponification reaction was found to be 858.9 ± 18 g.mol$^{-1}$.

### 3.1 Effect of reaction time on biodiesel yield

The effect of reaction time on biodiesel yield is shown in Figure 1. FAME content was low before 1.5 h. Reaction rate significantly increased after 1.5 h, and the reaction approached equilibrium at about 2.25 h. The reaction can be divided into three periods: induction, rapid reaction and equilibrium.

### Induction period

Before 1.5 hours, the reaction rate was slow. In the beginning, methanol and CaO were poured into the flask, then, preheated oil was added. In the beginning the catalyst was covered by oil instead of methanol since the system was left alone for 3-5 minutes in order to steady the temperature. Granados *et al.* [11] studied the reaction rates when CaO was firstly contacted with oil, methanol or biodiesel. The highest reaction was obtained when CaO was covered by biodiesel. On the contrary, CaO covered by oil resulted in the lowest reaction rate with a long induction period.

Once, CaO was covered by oil, methanol had to diffuse onto catalyst surface through oil layer for reaction to occur. During the induction period, methanol and oil were gradually mixed by magnetic stirring so the resistance of external diffusion gradually decreased.

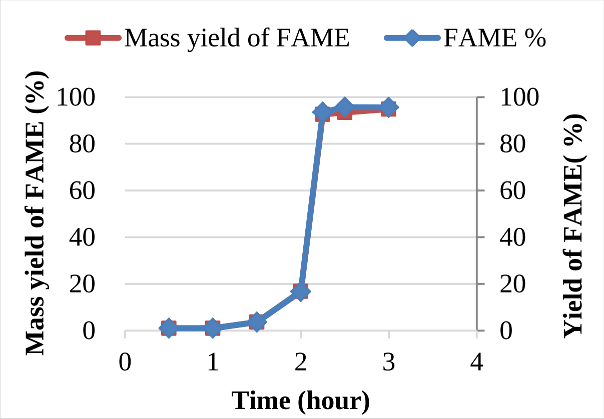

***Figure 1.*** *Effect of reaction time on FAME yield (%) in transesterification reaction of soybean oil, 3 wt.% catalyst, 60℃, methanol to oil molar ratio = 6*

### Rapid reaction period

It was observed that the reaction rate increased dramatically from 1.5 to 2.25 hours. During this period, both external diffusion and internal diffusion resistances seemed to be significantly reduced. This happened because as FAME was formed, oil and methanol can be mixed well. According to Granados *et al.* [11], biodiesel can be fully dissolved in both oil and methanol. Pores of catalyst are filled with FAME, methanol and oil are easier to access the catalyst surface. Thus, FAME that existed in the catalyst's pore can enhance the reaction rate effectively.

### Equilibrium period

When approaching equilibrium, prolonged reaction time did not have a the significant effect on FAME conversion [10, 11 12, 13, 14].

## 3.2 Effect of preheating time on biodiesel yield

Diffusion was the rate-limiting step in the initial transesterification reaction. The problem can be solved by preheating CaO and methanol before transesterification were carried out. Fig.2 shows the effect of preheating time on FAME yield.

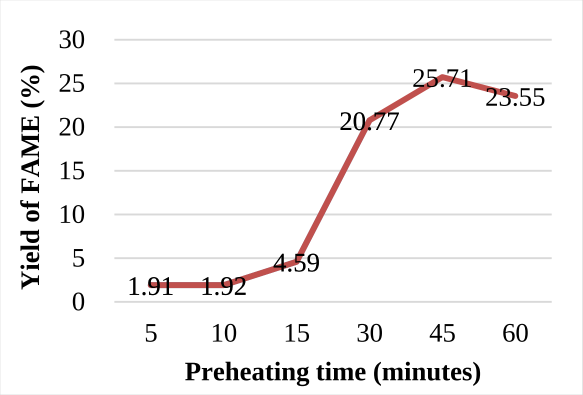

***Figure 2.*** *Effect of preheating time of CaO and MeOH on FAME yield, 3 wt.% catalyst at 60℃, methanol to oil molar ratio = 6, reaction time = 30 minutes.*

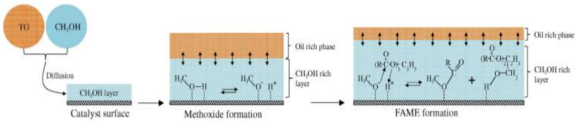

***Figure 3.*** *Mechanism of preheating and transesterification.*

At a preheating time less than 10 minutes, FAME yield of 1.91% was only a little higher than the non-preheating result (about 1%). This is because the catalyst can be covered by methanol following this preheating step. The mechanism of preheating and transesterification is illustrated in Figure 3 [15].

As preheating time was increased from 15 minutes to 30 minutes, FAME content increased from 4.59% to 20.77%, an increase of almost 4 times. Since the mass transfer rate depends on concentration difference, as methanol concentration on catalyst surface increased, the diffusion rate decreases. Therefore, there should be reasons other than mass transfer resistance.

The spent catalysts for 15 and 45 minutes preheating time were collected and analyzed by FTIR. The spectrum of the reference sample (Ca-M) showed important peaks at 2825 $cm^{-1}$ and 2920 $cm^{-1}$ which refers to $OCH_3^-$ and C-H stretching, respectively (Figure 4). It exhibited the same characteristic with spent catalyst preheated for 45 minutes (Figure 5). In addition, catalyst preheated for 15 minutes also had a tiny peak at the same wavelength region (2800 - 3000 cm$^{-1}$). It can be explained that some Ca-M were formed at 15 and 45 minutes preheating but the amount of Ca-M was still low based on the difference in catalyst weight before and after the reaction.

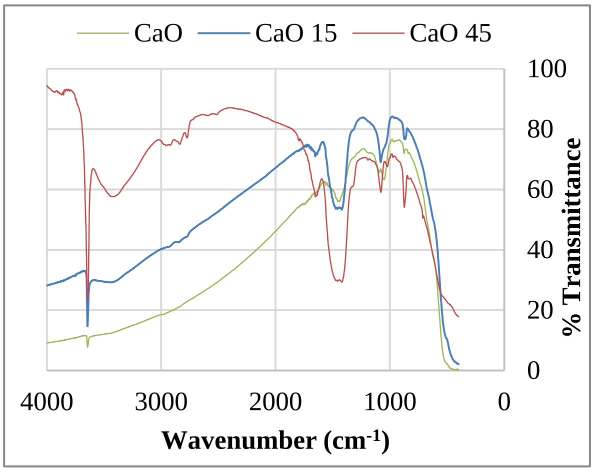

***Figure 4.*** *IR spectra of CaO and CaO preheated with methanol for 15 minutes and 45 minutes*

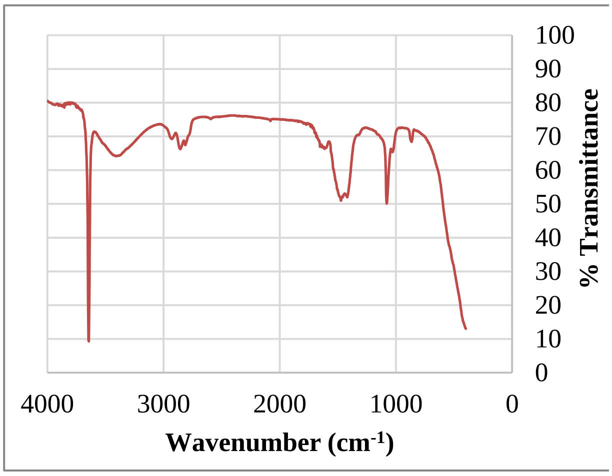

***Figure 5.*** *IR spectrum of Ca-M and CaO reacted with methanol for 2 hours.*

A slight decrease in FAME content was observed at 60 minutes preheating time. Longer preheating time led to some methanol loss. In spite of the condenser was used, it cannot avoid the loss of methanol by evaporating through the top of condenser. The function of preheating was to bring methanol onto catalyst surface and to create a little Ca-M which can be used as an initiating reagent (Figure 3). Longer preheating time (> 60 minutes) was not investigated, because FAME content seemed to reach the maximum at 45 minutes preheating.

### 3.3 Comparison of 15 and 45 minutes preheating time

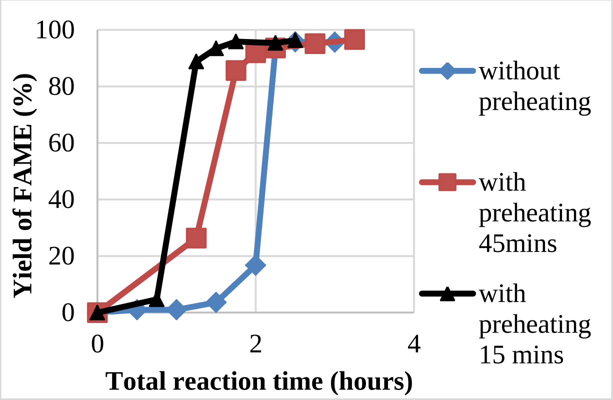

***Figure 6.*** *Effect of preheating time on FAME yield, 3 wt.% catalyst, 60℃, methanol to oil molar ratio = 6.*

A preheating time of 45 minutes was found to give the highest FAME yield (Figure 2). Figure 3 shows the effect of total reaction time (including preheating) on FAME yield. By using 15 minutes preheating, the total reaction time to reach high yield was 45 minutes, considerably less than that of without preheating. The reason was that there was a little Ca-M formed at 15 minutes preheating and FAME started to increase at this point. By shortening the preheating time to make the reaction continue to occur one after another. Figure 6 shows the equilibrium reaction times of 15 minutes preheating, 45 minutes preheating time and without preheating are 1.5, 2, and 2.25 hours, respectively.

## 4. CONCLUSIONS

In this study, three periods in the rate-time curve (induction period, rapid reaction period and equilibrium period) were reported when CaO was used as the catalyst for biodiesel production from soybean oil. According to literature, usually CaO was pretreated with methanol to form CaM as the initiator to accelerate the reaction rate of transesterification. This research found that the optimal preheating time and the optimal reaction time to reach the maximum yield of FAME is 15 minutes and 1.25 hours, respectively. Finally, there are some suggestions for further research such as the study of the reaction rate of transesterification of soybean oil using CaO as the catalyst, and modification of the surface of CaO to achieve high surface area and its application to other chemical reactions.

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