



# Transesterification of soybean oil to biodiesel using cement as a solid base catalyst

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## ABSTRACT

This work studies the recycling of cement as a catalyst in the production of biodiesel by transesterification of soybean oil with methanol. Literature survey showed that cement has never been studied as a solid catalyst in the transesterification of triglyceride. Concrete is a composite construction material composed of cement, aggregate, water, and chemical admixtures. In these composite, Portland cement was supposed to be an efficacious catalyst for biodiesel production. Therefore, the catalytic effects of calcination temperature, oil/alcohol ratio (mol/mol), and catalyst amount (wt% of oil) of hydrated cement were discussed. Finally, the waste concrete catalyst was successfully used in the transesterification reaction of soybean oil according to catalytic property of the cement catalyst.

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## 1. Introduction

In recent years, there has been increased focus on global warming and the depletion of resources caused by heavy consumption of fossil resources. In order to resolve these problems, biomass is increasingly gaining international attention as a source of renewable energy. Biodiesel is produced from vegetable oils by the transesterification reaction of triglycerides with methanol in the presence of a catalyst to yield the corresponding fatty acid methyl esters (FAME) and glycerol as the co-product. Although the homogeneous catalyzed biodiesel reaction is relatively fast and records high conversions, it has some serious drawbacks [1]. The catalyst cannot be recovered and must be neutralized and separated from the methyl ester phase at the end of the reaction that consequently generated large volume of wastewater. These problems have provided an impetus to the search of stable and more environmentally friendly solid catalysts. While searching for promising solid base catalysts, several attempts were made with alkali earth oxides such as CaO, SrO and BaO [2–4]. Alkali and alkali earth salts loaded on metal oxide such as KOH/Al<sub>2</sub>O<sub>3</sub> [5], KF/MgO [6], Sr(NO<sub>3</sub>)<sub>2</sub>/ZnO [7], Ca(NO<sub>3</sub>)<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> [8] and calcined Mg–Al hydrotalcites [9,10]. A variety of solid acids has already been tested such as carbon-based solid acid [11], WO<sub>3</sub>/ZrO<sub>2</sub> [12], SO<sub>4</sub>/ZrO<sub>2</sub> [13], SO<sub>4</sub>/TiO<sub>2</sub> [14], SO<sub>4</sub>/ZrO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> [15] and Nafion [16]. Their catalytic efficiency has been reviewed for methyl ester synthesis via both esterification of free fatty acid and transesterification of triglycerides.

Today, Portland cement is a widely used binder in concrete construction [17]. Waste arising from the construction sector construction and demolition waste (C&D) is also a relevant concern in the protection of the environment. The quantities of construction and demolition (C&D) wastes generated in Taiwan significantly rose to 1.27 million tons in 2009 (EPA, Taiwan) [18]. The most common way of disposing C&D waste is by landfill, which nevertheless creates large dumping sites of C&D waste resulting eco-damage. Therefore, an increasing strengthens law regulation in forms of prohibitions or special taxes against the C&D waste dumping sites were implemented in developed countries [19]. In this work, the application of cement as catalyst for biodiesel production not only provides a cost-effective and environmental friendly way of recycling the cement waste but also reduces the cost of biodiesel production.

The hydrated cement blocks were ground and calcinated for the transesterification reaction of soybean oil with methanol in a batch of reactor system. Catalytic activities of the prepared catalyst were investigated under different calcinated temperatures (150–950 °C), molar ratios of oil to methanol (1/6–1/24), and catalyst amount used. The catalysts were characterized by X-ray diffraction (XRD), scanning electron-microscopy (SEM), energy dispersive spectroscopy (EDS), and Hammett indicators.

## 2. Materials and methods

### 2.1. Materials and preparation of the catalyst

Soybean oil for cooking was obtained from the Great Wall Enterprise Co. (Taiwan). The methanol (ACS grade) was purchased

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from ECHO Chemical Co. (Taiwan). Waste concrete block was picked in the National Taichung University of Education. Model hydrated cement blocks were directly prepared by mixing Portland cement (Type I, Universal Cement Co., Taiwan) with water in ratio of 3/1 (W/W), and the resulting paste was stood to solid at room temperature for 28 days. Calcination was performed in a muffled furnace at various temperatures between 150 and 950 °C for 3 h under static air after crushing the hydrated cement block. Activities of the prepared catalyst were investigated under different calcinated temperatures, molar ratios of oil to methanol, and catalyst amount used.

## 2.2. Transesterification reaction procedure

The conversion of soybean oil to biodiesel was performed in a 250 ml flat-bottom flask equipped with a reflux condenser and a magnetic stirrer. The transesterification reaction of soybean oil and methanol was carried out in liquid phase under atmospheric pressure, at 65 °C for 3 h while stirring at 900 rpm. The timing of the reaction was initiated as soon as the mixture of methanol and the catalyst was added into the reactor. The effects of molar ratio of oil/methanol (1/6–1/24), catalyst/oil weight ratio (1–4 wt%) and different calcinated temperatures (150–950 °C) of the catalysts on the conversion of triglycerides to biodiesel were investigated. After the transesterification reaction, DI water was added into the reaction mixture to stop the reaction. A supernatant was filtrated through a common filter paper, and then excessive amount of methanol and water was evaporated before the analysis of FAME.

## 2.3. Instruments and analytical methods

The base strength of the samples ( $H_-$ ) was determined by using Hammett indicators [6]. About 50 mg of sample was shaken with 1 ml methanol solution of the Hammett indicator. Two hours were allowed to elapse for equilibrium to be reached under which no additional change of color took place. The basic strength is defined as being stronger than the weakest indicator, which exhibits a color change, and weaker than the strongest indicator that produces no color change. The concentrations of 0.02 mol/L bromthymol blue ( $H_- = 7.2$ ), phenolphthalein ( $H_- = 9.8$ ), 2,4-dinitroaniline ( $H_- = 15.0$ ) and 4-nitroaniline ( $H_- = 18.4$ ) were used for Hammett indicators. Methanol was used as a solvent. The characterization of catalysts were performed on a MAC MXP18 Powder X-ray diffractometer, using Cu K $\alpha$  radiation, over a  $2\theta$  range from 10° to 90° with a step size of 0.04° at a scanning speed of 3° min<sup>-1</sup>. The morphology and chemical composition of cement samples were investigated by using a JEOL JSM-7401F Field Emission SEM. Thermogravimetric analyses were carried out with a Seiko SSC 5000 instrument. The samples (10.6 mg) were heated from room temperature up to 1000 °C, with a scan rate of 5 °C/min, and under an air atmosphere stream (air flow = 80 ml/min) to ensure water desorption. The samples were analyzed as received (i.e. without any vacuum pre-treatment or special heat conditioning). The FAME concentration expressed as the biodiesel purity of the product was determined by gas chromatography (Thermo trace GC ultra, Thermo Co.) equipped with a flame ionization detector, a capillary column (Tr-biodiesel (F), Thermo Co., 30 m in length with 0.25 mm i.d. and 0.25  $\mu$ m film thickness), the programmed column oven, and a programmed temperature injector. The oven temperature program consisted of: start at 120 °C (keep 1 min), ramp at 30 °C/min to 220 °C (keep 1 min), then continue ramp at 10 °C/min to 250 °C (keep 1 min). The temperature of the programmed temperature injector was 90 °C for 0.05 min, programmed to 260 °C, at a rate of 10 °C/min. Nitrogen was as a carrier gas with a flow-rate of 2 ml/min. The amount of FAME could be calculated by the internal standard

(methyl heptadecanoate) method, according to Chinese National Standard 15051.

## 3. Results and discussion

### 3.1. Material characterization

In ordinary Portland cement (OPC), there are four major compounds: tricalcium silicate (3CaO·SiO<sub>2</sub>, C<sub>3</sub>S), dicalcium silicate (2CaO·SiO<sub>2</sub>, C<sub>2</sub>S), tetracalcium aluminoferrite (4CaO·Al<sub>2</sub>O<sub>3</sub>·Fe<sub>2</sub>O<sub>3</sub>, C<sub>4</sub>AF), and tricalcium aluminate (3CaO·Al<sub>2</sub>O<sub>3</sub>, C<sub>3</sub>A). Both C<sub>3</sub>S and C<sub>2</sub>S react with water (H) to form calcium silicate hydrate (CSH) and calcium hydroxide (CH) as their principal hydration products in the manner of 2C<sub>3</sub>S + 6H → C<sub>3</sub>S<sub>2</sub>H<sub>3</sub> + 3CH and 2C<sub>2</sub>S + 4H → C<sub>3</sub>S<sub>2</sub>H<sub>3</sub> + CH [20]. These abbreviations such as C<sub>3</sub>S, C<sub>2</sub>S and C<sub>4</sub>AF were defined from American Society of Civil Engineers. The formula of C<sub>3</sub>S<sub>2</sub>H<sub>3</sub> is a rough approximation, and more than one form of this hydrate is possible. Fig. 1 shows the XRD patterns of the hydrated cements being calcined at 250–650 °C for 3 h. The main peaks corresponding to Alite (C<sub>3</sub>S, JCPDS 42-0551), Belite (C<sub>2</sub>S, JCPDS 87-1257), Ca(OH)<sub>2</sub> (CH, JCPDS 87-0673), CaO (JCPDS 77-2376), and CaCO<sub>3</sub> (JCPDS 86-2342) are the main components of cement. Though cement is a complex material and the main peaks of XRD pattern are usually overlaid to one another, the major phases change of Ca(OH)<sub>2</sub> in the cement is obvious when the calcination is performed. The catalyst calcined at 250 °C shows peaks at 18.0°, 34.1°, 47.3° and 50.8° due to the presence of Ca(OH)<sub>2</sub>. Most of diffraction peaks related to CaO are observed at 32.2°, 37.4° and 53.9° during calcinations at 450–650 °C. CaO is more catalytic than Ca(OH)<sub>2</sub> for transesterification reaction. Table 1 summarizes the base strengths of hydrated cement and waste concrete with different calcinated temperatures. The results agree to the XRD experiment and shows that hydrated cement and waste concrete calcined above 450 °C are active solid base catalysts with  $H_-$  in the range of 15–18.4.

Fig. 2 shows typical SEM-EDS image of the cement and concrete catalyst giving dense particles with similar morphology but different heterogeneous distribution of particle sizes. The particle size of concrete is larger than that of cement as they have different cement production processes and sand particles are larger than cement. The cement and concrete catalyst are generally considered rather less-porous material, and are mainly composed of O, Ca, Si, Mg, Fe, and Al elements, corresponding to the main stocks of cement. These include limestone (CaCO<sub>3</sub>), silica sand (SiO<sub>2</sub>), iron oxides (Fe<sub>2</sub>O<sub>3</sub>) and clay (aluminum silicate and magnesium silicate). Fig. 3 shows the TG and differential thermal analysis (DTA) thermogram of the cement catalyst. As can be seen

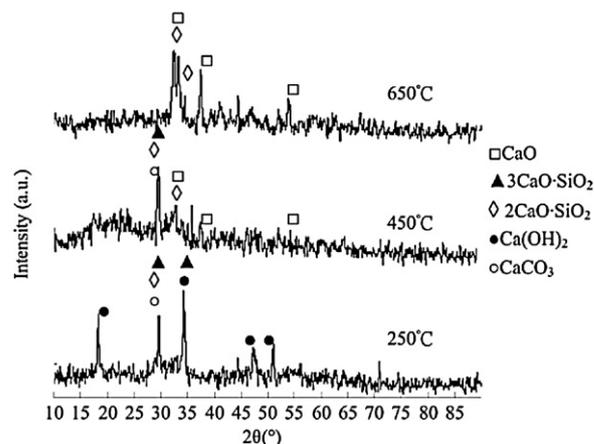


Fig. 1. XRD patterns obtained by calcining hydrated cement in the range of 250–650 °C.

**Table 1**  
Base strengths of cement and concrete with different calcinated temperatures.

Catalyst	Calcinated temperature (°C)	Base site strength ( $H_-$ )
Cement	150	$7.2 < H_- < 9.8$
Cement	250	$7.2 < H_- < 9.8$
Cement	350	$9.8 < H_- < 15.0$
Cement	450	$15 < H_- < 18.4$
Cement	650	$15 < H_- < 18.4$
Cement	850	$15 < H_- < 18.4$
Concrete	650	$15 < H_- < 18.4$

from this figure, three stages of decomposition are distinguishable in different temperature zones. Thermal assessment for the cement paste on the temperature effects have been reported [20,21]. It is generally considered that the evaporable water is completely eliminated at 120 °C. Above 110 °C, the gypsum and the ettringite start decomposition, and the loss of water from part of the carboaluminate hydrates take place below 170 °C. CSH and carboaluminate hydrates undergoes dehydration reaction between 180 and 300 °C and the dehydroxylation reaction of portlandite takes place around 450–550 °C. Then, the calcium carbonate began to decompose beyond 700 °C.

### 3.2. Parameters that effect the transesterification reaction

The investigated variables included the calcination temperatures of the catalyst, the oil/alcohol ratio (mol/mol), and catalyst amount (wt% of oil). The activities of catalyst for this reaction are plotted corresponding to the calcination temperatures as shown in Fig. 4. The activity profiles clearly indicated that the activities of the cement catalyst strongly depended on the calcination temperatures. A conversion of 96.1–98.8% was obtained in the presence of cement sample calcined above 450 °C. This agrees with TGA–DTA curves (Fig. 3) suggesting attribution of the dehydroxylation reaction of calcium hydroxide [20,21] responsible for the

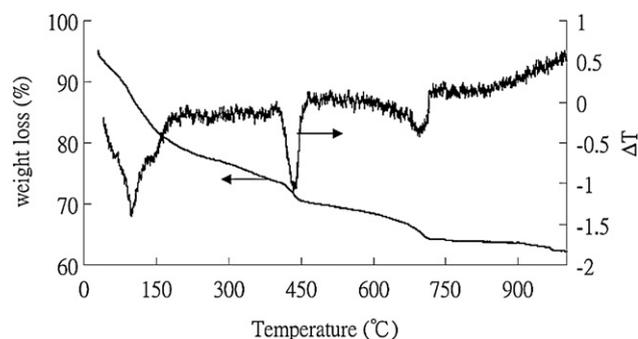


Fig. 3. TG and DTA curves for the freshly cement sample.

high reactivity of the catalysts towards transesterification reaction. A biodiesel conversion of <16.0% was gained in the presence of cement catalyst calcined <450 °C. This also agrees with the base strength of the samples in Table 1. When the 2,4-dinitroaniline indicator was added into the methanol solution of samples calcined above 450 °C, the color slightly changed. It was assumed that the samples contained some basic sites of  $H_- > 15.0$  on the surface, causing the catalysts for the high reactivity towards transesterification reaction.

The effect of the cement catalyst amount on the conversion was also investigated. As shown in Fig. 5, the conversion increased as the catalyst amount increased from 1–5%. The conversion reached a plateau value at the catalyst weight percent between 4 and 5%. Stoichiometrically, the transesterification of soybean oil requires three moles of methanol for each mole of oil. Since transesterification reaction is a reversible reaction, excess methanol would shift the equilibrium towards the direction of FAME formation. As evidence from Fig. 6, when the methanol loading increased, the conversion increased considerably. The maximum conversion ratio was 98.5% at the oil/methanol molar ratio of 1:24.

After the transesterification reaction was completed, the samples were recovered by simple decantation. The remaining catalyst in the reactor was applied for the next batch of transesterification reaction. The reusability of catalyst is depicted in Fig. 7, and the conversion ratio dropped significantly after 5 cycles. The decrease in the activity of the catalyst might be due to the reaction between calcium oxide and glycerol in the transesterification reaction and to the formation of calcium diglyceride which has been described [22]. Glycerol covering the surface of catalyst was also considered as the reason for activity loss. This test shows the benefits of the reuse characteristics of these catalysts, however, their lifetime in an industrial setting should be significantly prolonged to be practical.

The solubility of the catalysts is also a very important factor that should be taken into account to correctly interpret their

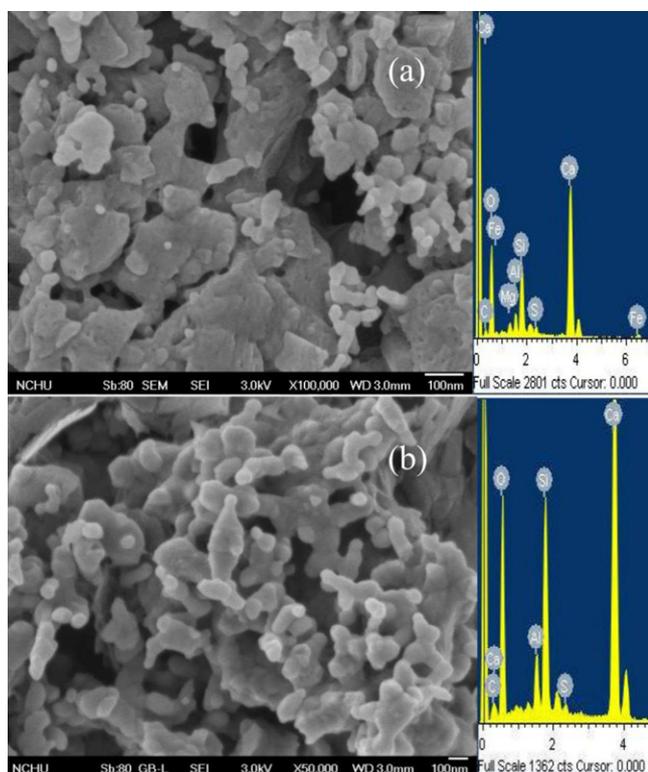


Fig. 2. SEM–EDS images of cement calcining at 750 °C (a) and concrete calcining at 650 °C (b).

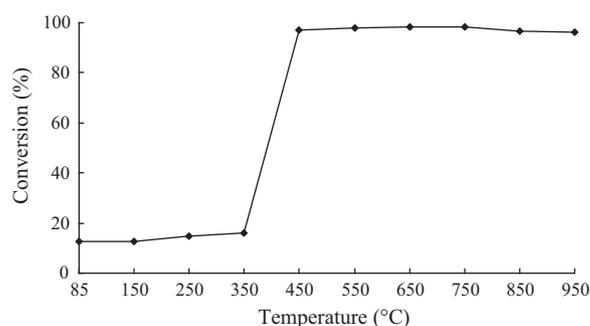
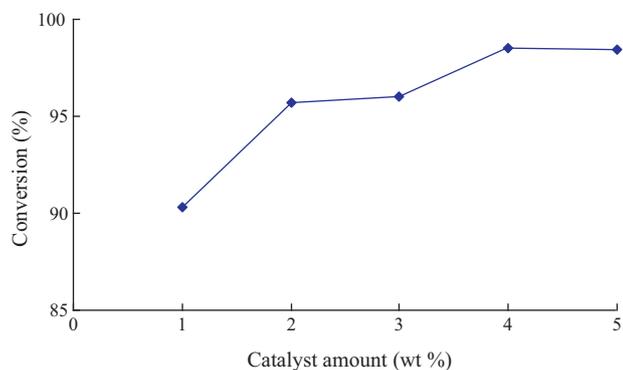


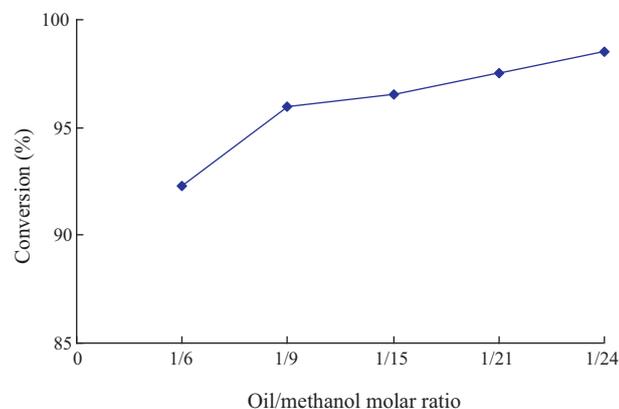
Fig. 4. Influence of calcination temperature on the conversion. Reaction conditions oil/methanol molar ratio 1/24, catalyst amount 4%, reaction time 3 h, reaction temperature 65 °C.



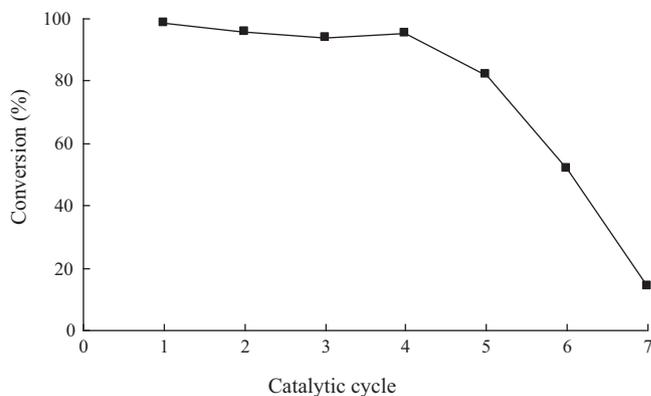
**Fig. 5.** Influence of catalyst amount on the conversion. Reaction conditions: calcinated temperature 650 °C, oil/methanol molar ratio 1/24, reaction time 3 h, reaction temperature 65 °C.

performance and assess their practical interest. If the solid catalyst becomes partly dissolved additional steps would be required during the refining of the produced biodiesel and glycerol thus complicating the fabrication process. Since leached active species could be responsible for the catalytic activity, the homogeneous contribution must be checked. In an attempt to clarify this point, the following experiment was carried out [23]. The activated cement was placed in contact with methanol and kept under stirring conditions (900 rpm) at 65 °C for 3 h. Then the stirring was stopped, the solid was filtered out, and the clear methanol solution was placed in contact with soybean oil to finish transesterification reaction. In other words, the transesterification reaction was carried out in the absence of solid catalyst but in the presence of the leached active species. After 3 h, this homogeneous reaction was stopped and the methyl ester conversion achieved was 1.3%. In contrast to the same reaction condition of heterogeneous reaction, the methyl ester conversion achieved was 98.5%. This result confirms the leaching of cement species in the presence of methanol and the homogeneous contribution would be slightly responsible for the activity of the cement catalyst.

Finally, the waste concrete was successfully tested in the transesterification reaction of soybean oil. It is known that the bonding strength of concrete can be weakened by dehydration due to heating [24]. Therefore, heating a concrete can weaken the interface between grains and thereby promote preferential breakage along the grain boundaries. After waste concrete blocks were calcined at 900 °C for 4 h, the binder of concrete (hydrated cement) was broken, and the coarse aggregate could be easily separated from cement and the fine aggregate. Then cement and



**Fig. 6.** Influence of oil/methanol molar ratio on the conversion. Reaction conditions: calcinated temperature 650 °C, catalyst amount 4%, reaction time 3 h, reaction temperature 65 °C.



**Fig. 7.** Effect of the reuse of catalysts on the conversion. Reaction conditions: calcinated temperature 650 °C, oil/methanol molar ratio 1/24, catalyst amount 4%, reaction time 3 h, reaction temperature 65 °C.

the fine aggregate were used as a catalyst together due to it is difficult to separate from each other. The waste concrete catalyst (cement and the fine aggregate) was successfully used in the transesterification reaction of soybean oil according to catalytic property of the cement catalyst, *i.e.* calcination temperature 650 °C for 3 h, reaction temperature 65 °C, oil/methanol molar ratio 1/24, the fatty acid methyl esters conversion could reach 97.6% after 3 h reaction. The 32.8 wt% catalyst amount was used due to the fine aggregate was contained in the catalyst. The organic chemical admixtures and fine aggregate did not affect the transesterification reaction due to it was burned down and neutral base strength, respectively.

#### 4. Conclusions

In order to utilize waste concrete as a catalyst for biodiesel production, thermally activated hydrated cement has been carefully discussed as a catalyst in the transesterification of soybean oil into FAME, with more than 98% FAME conversion. Waste concrete catalyst was also successfully tested in the transesterification reaction of soybean oil. Under the optimal conditions of calcination temperature 650 °C for 3 h, reaction temperature 65 °C, catalyst amount 32.8 wt% (cement and fine aggregate) and oil/methanol molar ratio 1/24, the fatty acid methyl esters conversion could reach 97.6% after 3 h reaction. Thermal decomposition is an efficient method to separate coarse aggregate from concrete and can be easy to practice in industry.

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