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Transesterification of Soybean Oil Catalyzed by Calcium Hydroxide which Obtained from Hydrolysis Reaction of Calcium Carbide

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Calcium carbide residue (CCR) was investigated in transesterification reaction of triglycerides to determine its viability as a solid catalyst for biodiesel synthesis. Literature survey showed that CCR has never been studied as a solid catalyst in the transesterification of triglyceride. The scope of the study includes the effects of CCR calcination temperature, calcination time, the alcohol/oil molar ratio, the catalyst amount (wt % of oil) and the reaction time. The relationship between chemical composition and catalytic activity of waste cement was also investigated. These CCR catalysts, thermally activated at 600 °C, can give rise to fatty acid methyl esters (FAME) purity higher than 99.5%, after 3 h of reaction, when oil/methanol molar ratio of 1/12 and 1 wt % of the catalyst were employed. Application of CCR as catalyst for biodiesel production in this study may not only provide a cost-effective and environment friendly way of recycling CCR waste but also reduce hopefully the cost of biodiesel production.

Keywords: Biodiesel; Solid catalyst; Calcium carbide residue; Transesterification.

INTRODUCTION

Recently, the global warming issue due to the heavy consumption of fossil resources and the depletion of natural resources has gained increasing concerns. For the considerations of sustainable development, biomass is increasingly catching international attention as a source of renewable energy. Generally speaking, biodiesel is a mixture product of FAME obtained from plant seed's oils by the transesterification reaction. This reaction takes place when the triglyceride of plant seed's oil was heated with methanol in the presence of catalyst and the product mixtures are the corresponding FAME and the glycerol. Although transesterification reaction is relatively fast and records high conversions in homogeneous catalyst system, it has some serious drawbacks[1] that the catalyst not only cannot be recovered and must be neutralized but also the separation of FAME from catalyst during the reaction process generates large volume of wastewater. These problems have provided an impetus to the search of stable and more environmentally friendly solid catalysts.[2] Literature survey indicated that alkali earth oxides are the main type of solid catalyst applied to the transesterification reaction, such as CaO, SrO and BaO.[3-5] Also alkali metal or alkali earth salts loaded on metal oxide such as: KOH/Al_2O_3,[6] KF/MgO,[7] $Sr(NO)_3/ZnO$,[8] $Ca(NO_3)_2/Al_2O_3$ [9] and calcined Mg-Al hydrotalcites[10-11] are commonly seen for transesterification reactions in recent years. Those catalysts mentioned above are classified as base solid catalysts; other acid solid catalysts have also been studied such as carbon-based solid acid,[12] WO_3/ZrO_2,[13] SO_4/ZrO_2,[14] SO_4/TiO_2 [15] and Nafion.[16]

Calcium carbide residue (CCR) is a by-product of acetylene production through the hydrolysis of calcium carbide. CaC_2 reacts with water to produce C_2H_2 gas, and CCR waste, namely $Ca(OH)_2$, is ordinarily landfilled outside the chlor-alkali plants. Although not being classified as dangerous/hazardous, its managing and disposal require special caution, since the highly basic sludge pH > 12) can also contain dangerous heavy metals (Mg, Br, Sr, Cd, Cu,

Pb, Fe, Mn, Ni and Zn).[17] Large amount of CCR not only accounts for the need of large area for land fielding, but also may results pollution to the field and their water source nearby. Therefore, how to make these CCR become useful resource is a matter of great urgency. Some efforts have been made to recycle CCR waste as a part of cement raw materials[18] and as a cementing paste.[19] Application of CCR as catalyst for biodiesel production in this study not only provides a cost-effective and environment friendly way of recycling CCR waste but also hopefully reduce the cost of biodiesel production.

EXPERIMENTAL
Materials and Methods

Soybean oil for cooking was obtained from the Great Wall Enterprise Co. (Taiwan). The methanol (ACS grade) was purchased from ECHO Chemical Co. (Taiwan). Model CCR were directly prepared by hydrolysis reaction of calcium carbide (Hua Xing Chemical Co., Taiwan). After hydrolysis reaction, the resulting CCR was calcinated at 130-900 °C for 1-5 hrs under static air in a muffled furnace for the transesterification reaction of soybean oil with methanol in a batch reactor. The activities of prepared catalyst were investigated under different calcinated temperatures, calcinated times, oil/methanol molar ratios, and catalyst amount used. The catalysts were characterized by X-ray diffraction (XRD), TG and differential thermal analysis (TGA-DTA), scanning electron-microscopy (SEM), and energy dispersive spectroscopy (EDS).

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 reactor was initially filled with 25 g of soybean oil, which was heated to 65 °C for 1-5 hrs 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 to methanol (1:6-1:18), catalyst/oil weight ratio (1-5 wt %), and different calcination time (1-5 hrs) and different calcination temperatures (130-900 °C) of the catalysts on the conversion yield of triglycerides to biodiesel were investigated. All of the experiments were performed under atmospheric pressure. After the transesterification reaction, DI Water was added into the reaction mixture to stop the reaction. The biodiesel and glycerol layers exhibit different densities of 0.86 and 1.126 g/cm^3, respectively,

and thus could be separated easily from each other. A supernatant was filtrated through a common filter paper, and then excessive amount of methanol was evaporated before the analysis of FAME.

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 μm 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^{-1} to 220 °C (keep 1 min), then continue ramp at 10 °C min^{-1} 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^{-1}. Nitrogen was as a carrier gas with a flow-rate of 2 mL min^{-1}. The amount of FAME could be calculated by the internal standard (methyl heptadecanoate) method, according to method CNS 15051.

The characterization of catalysts were performed on a MAC MXP18 Podwer X-ray diffractometer, using Cu Kα radiation, over a 2θ range from 20 to 80° with a step size of 0.04° at a scanning speed of 2° min^{-1}. The morphology and chemical composition of individual phases of the polished 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 (11.42 mg) were heated from room temperature up to 1000 °C, with a scan rate of 5 °C min^{-1}, and under an air atmosphere stream (air flow = 80 mL min^{-1}) to ensure water desorption. The samples were analyzed as received (i.e. without any vacuum pre-treatment or special heat conditioning).

RESULTS AND DISCUSSION

The CCR is generated as an aqueous slurry and is essentially composed of calcium hydroxide ($Ca(OH)_2 \approx$ 85-95%) with minor amount of calcium carbonate ($CaCO_3 \approx$ 1-10%), unreacted carbon and silicates (1-3%).[20] Fig. 1 shows the XRD patterns of CCR catalysts. CCR catalysts calcined below 600 °C present XRD patterns identical to that of $Ca(OH)_2$ (as referred to PDF card no. 841270). CCR catalysts calcined above 600 °C show XRD patterns identical to that of CaO (as referred to PDF card no. 772376),

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corresponding to the dehydroxylation of $Ca(OH)_2$. Figure 2 shows the TG and differential thermal analysis (DTA) thermogram of the CCR catalyst. As shown from this figure, two stages of decomposition can be distinguished in different temperature zones. It can be seen that $Ca(OH)_2$ begins to decompose at about 450 °C, and a clear endothermic peak appears between 380 and 500 °C. Then, the calcium carbonate begins to decompose, and this appears in Fig. 2 as a steep slope between 640 and 760 °C. The result of the TG analysis indicates that the CCR catalyst is stable below 350 °C.

Fig. 3 shows typical SEM-EDS image of the CCR giving dense particles with heterogeneous distribution of particle sizes. The smaller size of the grains aggregate higher yields on specific surface areas, hence the specific surface areas of CCR calcined at 600 °C is higher than that at 900 °C. The CCR is generally considered as rather low-porous material, and is mainly composed of O and Ca elements, corresponding to the main stock of CCR.

The investigated variables include calcination temperatures and period for the catalyst, alcohol/oil molar ratio, catalyst amount (wt % of oil) and reaction time. The activities of cat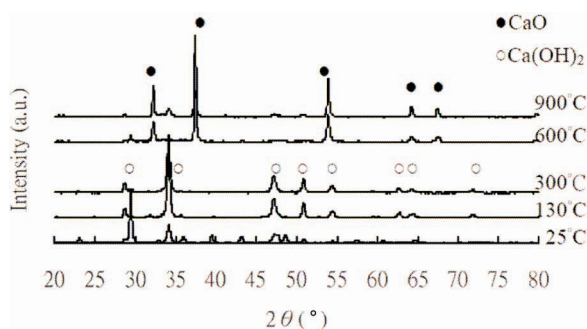alyst for this reaction are plotted correspond-ing to the calcination temperatures as shown in the Fig. 4, which clearly indicates that the activities of the CCR catalyst strongly depend on calcination temperatures. The kinetic model describing the behavior of the dehydration reaction of calcium hydroxide in the range of temperatures 330-450 °C is reported.[21] Thus in this study, when CCR is calcinated at 600 °C, significantly higher catalytic activity is observed. This suggests the dehydroxylation reaction of calcium hydroxide responsible for the high reactivity of the catalysts towards transesterification reaction. When calcium hydroxide is thermally treated at intermediate temperatures (350-550 °C), the solid product shows a higher specific surface area than does the initial reagent.[22] Surface generation depends on the kinetics of dehydration that, at
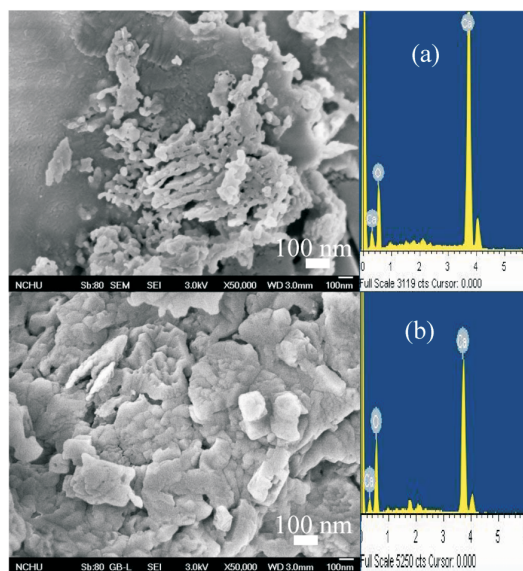

Fig. 3. SEM-EDS imagine of CCR calcining at (a) 600 °C, (b) 900 °C.

Fig. 1. XRD patterns obtained by calcining CCR at 25-900 °C for 2 hrs.
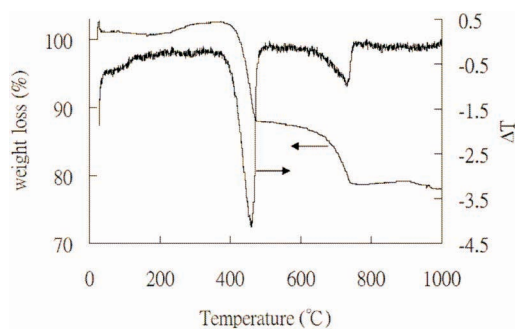
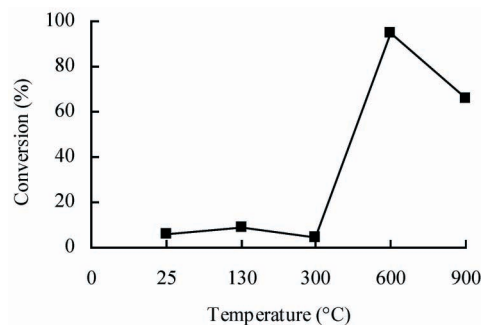Fig. 2. TG and DTA curves for the freshly CCR.

Fig. 4. Influence of calcination temperature on the conversion. Reaction conditions: oil/methanol molar ratio 1:12, catalyst amount 1%, reaction time 2 h, reaction temperature 65 °C.

long time or when decomposition of the initial solid taking place at high temperatures, changes on the surface area and porosity due to sintering phenomena are of considerable importance, decreasing the specific surface area and resulting in the reactivity with gases. Thus in this study, when CCR is calcinated at 900 °C, lower catalytic activity is observed in Fig. 4. This suggests a lower specific surface area when decomposition of CRC takes place at high temperatures above 900 °C.

As shown in Fig. 5, the conversion is increased as the calcinated time increases from 0.5-4 hrs, suggesting that the dehydroxylation reaction of calcium hydroxide is finished during 2 hrs at 600 °C. The conversion is obviously decreased when CCR is calcinated at 600 °C for 5 hrs, suggesting a lower specific surface area when decomposition of CRC takes place at 600 °C over 5 hrs.

The effect of the CCR catalyst amount on the conversion is also investigated. The catalyst amount is varied in the range of 0.5-5%. As shown in Fig. 6, the conversion is increased as the catalyst amount increases from 0.5 to 5%.
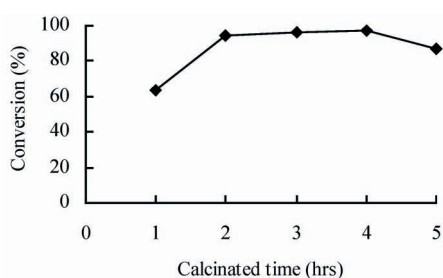

Fig. 5. Influence of calcination time on the conversion. Reaction conditions: calcinated temperature 600 °C, oil/methanol molar ratio 1:12, catalyst amount 1%, reaction time 2 h, reaction temperature 65 °C.
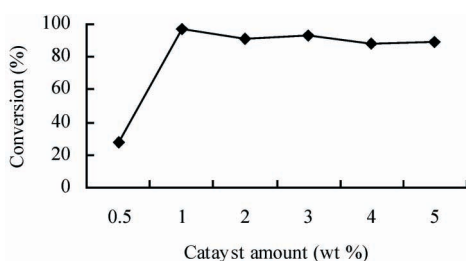

Fig. 6. Influence of catalyst amount on the conversion. Reaction conditions: Reaction conditions: calcinated temperature 600 °C, calcinated time 4 h, oil/methanol molar ratio 1:12, reaction time 2 h, reaction temperature 65 °C.

The conversion reaches a plateau value at the catalyst weight percent above 1%.

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 FAME formation. Figure 7 shows the effect of molar ratio of oil/methanol on the conversion of FAMEs. From 1:6 to 1:12 of molar ratio of oil to methanol, conversion of FAMEs increases. The maximum FAMEs conversion is 97.3%, when molar ratio is 1:12. After the molar ratio is over 1:12, the FAMEs conversion commences to descend slightly with molar ratio mounting up. This might be because the increment of methanol engendered augment of FAMEs conversion from 1:6 to 1:12 of molar ratio. However, with molar ratio mounting up, higher molar ratio lowers the relative concentration of soybean oil in reaction mixture. Low concentration of soybean oil brings low reaction rate, which also changes the equilibrium direction of reaction. Thus, 1:12 is accepted as the best molar ratio.

In Fig. 8, the conversion versus reaction time are presented. It can be seen that the conversion is increased in the reaction time range between 1 to 3 hrs, and thereafter the reaction time is over 3 hrs, the FAMEs conversion commences to descend slightly with reaction time mounting up. This suggests that the glycerol released during the transesterification reaction reacts with CaO forming Ca glyceroxides and loses its catalytic activity.[23]

Fig. 9 shows the trend for biodiesel conversion change obtained when the temperature is varied. Biodiesel conversion increases over the course of temperature. Normally, a
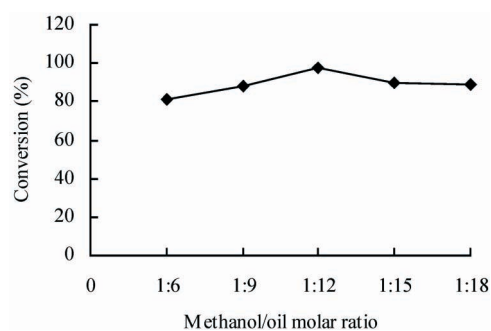

Fig. 7. Influence of oil/methanol molar ratio on the conversion. Reaction conditions: calcinated temperature 600 °C, calcinated time 4 h, catalyst amount 1%, reaction time 2 h, reaction temperature 65 °C.

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relatively high reaction temperature is required for heterogeneous system in order to increase the mass transfer rate between reactant molecules and catalyst. This is due to the existence of initial 3-phase mixture of oil–methanol–solid catalyst. The conversion obviously increases at 65 °C, as methanol boiling helps increase mass and heat transfer rate between reactant molecules and catalyst.

In Fig. 10, the main concept of CCR catalyst for biodiesel production is presented. Calcium carbide reacts with
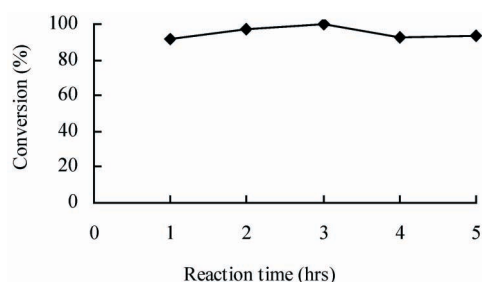

Fig. 8. Influence of reaction time on the conversion. Reaction conditions: calcinated temperature 600 °C, calcinated time 4 h, catalyst amount 1%, oil/methanol molar ratio 1:12, reaction temperature 65 °C.
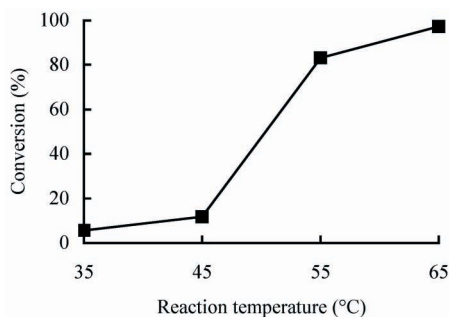

Fig. 9. Influence of reaction temperature on the conversion. Reaction conditions: calcinated temperature 600 °C, calcinated time 4 h, catalyst amount 1%, oil/methanol molar ratio 1:12.
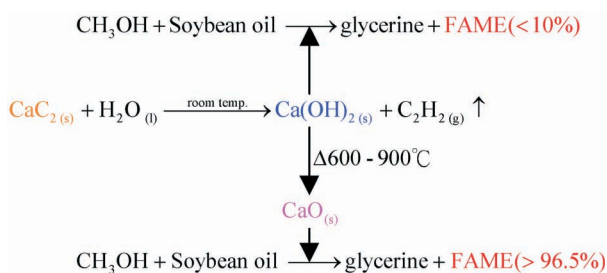

Fig. 10. The main concept of CCR catalyst for biodiesel production.

water to form calcium carbide residue (CCR: main composition is calcium hydroxide) and acetylene. CCR is calcined to form calcium oxide at 600 °C, which is the base catalyst for transesterification reaction. Calcinated CCR exhibits highly catalytic to yield FAME for more than 96.5%.

CONCLUSIONS

Calcinated CCR exhibited highly catalytic activity for the transesterification reaction of soybean oil with methanol to yield corresponding FAME mixtures, ie biodiesel, in more than 99.5% conversion. The study results showed that the optimum reaction conditions are when the methanol and soy-bean oil mixture are at the molar ratio of 12 to 1 with 1% of CCR catalyst and are heated to 65 °C for 3 hr's. We expect such environmentally benign CCR catalysts should seek for applications in a wide range of other base-catalyzed important organic reactions.

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