Effect of barium loading on CaO derived from waste egg shell heterogeneous catalyst for canola oil biodiesel

Jakkrapong Jitjamnong^{1,*}

¹Petroleum Technology Department, Faculty of Industrial Education and Technology, Rajamangala University of Technology Srivijaya, Songkhla, Thailand

Abstract. The purpose of this research was to investigate the catalytic activity of Ba loading on calcium oxide (CaO) catalyst by varying the amount of barium added during the synthesis: 5-15 wt%. The waste egg shells were utilized as a CaO heterogeneous catalyst by calcined at 900 °C for 2 h. The Ba/CaO catalysts were prepared by impregnation method and were used as a catalyst in transesterification reaction of canola oil via microwave irradiation under microwave power 300 W. The characterization of catalyst and FAME composition of biodiesel were determined by X-ray fluorescence (XRF), scanning electron microscope (SEM), Fourier transform infrared spectrometer (FTIR), and gas chromatography (GC-FID). The conditions of biodiesel production were operated at 60 °C, 3 wt% of catalyst loading, 9:1 methanol-to-canola oil ratio, and microwave irradiation power was 300W for 2 min. The experimental results found that, the waste egg shells consist mainly of CaCO₃, which was decomposed to CaO more than 88 wt% after calcination step. The 15 wt% Ba/CaO catalysts exhibited the best catalytic performance with the FAME conversion higher than 97.68%.

1 Introduction

In recent year, the increasing exhaust of fossil based fuel and energy consumption due to rapidly increase of population and the expansion of economic. To solve these problems, biodiesel is an alternative energy becomes more significant due to biodegradable, renewable, low emission of SO_x and CO_x, non-toxic, and environmentally-friendly fuel, which can substitute petro-diesel. Biodiesel is a mixture of mono alkyl esters of long chain fatty acid methyl ester (FAME) can be synthesized from new and used plant oil or animal fats with an alcohol (methanol or ethanol) via transesterification [1-2]. In general, homogeneous base catalysts such as potassium hydroxide (KOH) or sodium hydroxide (NaOH) are some main disadvantages related to corrosion, non-reuse, and difficult to remove catalyst from the reactant mixture and consequently influences the abundant of waste cleaning water. However, the use of heterogeneous catalysts (solid based) has demonstrated higher catalysis, reused for the many production cycle time, easily separated out from the reaction system, less corrosive, and more environmentally friendly [3]. Calcium oxide (CaO) as heterogeneous catalyst has attracted much attention for transesterification of biodiesel production due to its high activity, low cost, and low solubility in biodiesel and methanol [4]. Several literature have studied the main resource of CaO from waste materials as heterogeneous catalyst such as crab shell [5], shrimp shell [6], river

snail shell [7], animal bones [8], and egg shell [4,9] etc. Several studies have reported that the catalytic activity of the catalyst was strongly dependent on the basicity [10]. Notably, bi-functional heterogeneous base catalysts from alkaline-earth oxides had high basicity, which was improved the catalytic activity for biodiesel production. BaO had highly basic sites and seems to be appropriate base catalyst in the transesterification process [11].

The present framework was determined the effect of catalyst doped with barium on CaO derived from waste egg shells as environment-friendly heterogeneous catalyst. The synthesized catalysts were prepared by impregnation method. The biodiesel production was carried out with transesterification of canola oil as starting material and was applied microwave irradiation in the chemical reaction. The prepared catalysts were evaluated by X-ray fluorescence (XRF), scanning electron microscope (SEM) with an energy dispersive spectroscopy (EDS), and Fourier transform infrared spectrometer (FTIR). The biodiesel products were investigated by gas chromatography (GC-FID).

2 Experimental

2.1 Materials

The canola oil was used as feedstock for transesterification, procured from Lam Soon Co. Ltd.,

* Corresponding author: Alekjakkrapong@gmail.com

Thailand. The waste egg shells as a source of CaO, were collected from local areas of Songkhla, Thailand. The powder of Barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, 99%) analytical grade reagent was bought from Ajax Finechem Pty Ltd. All of the chemicals were analytical grade.

2.2 Catalysts preparation

The waste egg shells were carefully rinsed with hot distillate water to remove the edible organic adhered to the egg shell, and was dried at 120 °C in an oven overnight. Then, the dried waste egg shells were grounded to powder. The powder egg shells were calcined in furnace at 900 °C for 2 h, which calcium carbonate was decomposed to calcium oxide, and are kept in dessicator. Synthesized the 5 wt% Ba/CaO, 2.66 g of barium chloride was mixed with distillate water and stirred for 15 min to become homogeneous. An aqueous solution containing barium chloride was impregnated on 50 g of CaO and kept for 12 h at room temperature. Next, the catalyst was dried at 120 °C for 24 h to remove absorbed water, and last, calcined at 900 °C for 4 h. The same procedure is applied for preparation of 10 and 15 wt% Ba/CaO catalysts.

2.3 Catalyst characterization

The actual element compositions of calcined waste egg shell were measured by X-ray fluorescence spectrometer (XRF) (PW 2400, Philips, Netherlands). The chemical composition of neat calcium oxide derived from waste egg shells was analyzed using Thermo Nicolet Fourier Transform Infrared spectrometer (FTIR) Nexus 670 model. The sample was recorded in absorbance mode at 32 scans with a resolution of 4 cm^{-1} by KBr pressed disks. The frequency range was from 650 to 4000 cm^{-1} . The particle morphology and surface texture of Ba supported on CaO were studied using scanning electron microscopy (SEM). The SEM images of sample were recorded with an energy dispersive spectroscopy (EDS) equipped (Oxford, Aztec).

2.4 Biodiesel production

100 g of canola oil was added to the glass equipped and plated at heater, which was operated at 60 °C. 3 g of calcined Ba/CaO (3 wt% compared to the starting vegetable oil) and methanol (9:1 methanol-to-canola oil ratio) was added into the glass equipped under agitation speed of 300 rpm with magnetic stirrer for 10 min. After that, the mixed solution was carried out under household microwave oven with a microwave irradiation power was 300W for 2 min. After transesterification, the catalyst was collected from mixture by filtration. The canola oil biodiesel and glycerol was separated by separatory funnel. Biodiesel was cleaned with hot distillate water at 65°C until pH was neutral in order to obtained pure biodiesel. Biodiesel was preserved in the

glass bottle with sodium sulphate anhydrous to remove the absorbed excess water.

2.5 Canola oil-derived FAME analysis

The fatty acid methyl ester compositions of canola oil-derived biodiesel were analyzed by chromatograph (Hewlett Packard 5890 Series II) equipped with FID detector (GC-FID). The GC-FID conditions were carried out by helium (99.99%) as a carrier gas with a flow rate of 70 ml/min, 200°C of injector temperature with a split ratio at 75:1, and the temperature detector was set at 230 °C. 0.2 μL of fatty acids was injected into an oven at 130 °C. An isothermal time was held 2 min, and the oven was raised up to 220 °C with a rate of 2°C/min, and held for 15 min with analytical time was 62 min.

3 Results and discussion

3.1 Catalyst characterization

Table 1 shows the chemical compositions of calcined waste egg shells. Note that the major component is CaO approximately 88.29 wt%. This result clearly shows that the CaCO_3 from egg shells powder was decomposed to CaO after calcinations method. Nevertheless, the minor components of prepared catalyst are MgO, SiO_2 , P_2O_5 , SO_3 , and SrO_3 was formed.

FTIR spectra of heterogeneous CaO catalyst as synthesized from waste egg shells which is illustrated in Figure 1. For the carbonyl groups, a broad transmission in the carbonate region can be observed at 871 and 1444 cm^{-1} , respectively. This result exhibited the CaCO_3 phase in starting material (waste egg shells) and was transformed to CaO after calcination at 900 °C for 2 h. The intense band at 3641 cm^{-1} was assigned to the hydroxyl group stretching of $\text{Ca}(\text{OH})_2$, which is identified to the absorption of atmospheric moisture on the surface of CaO catalyst [11,12].

The surface morphology of calcined catalysts were evaluated using SEM equipped (Figure 2). The neat CaO (Figure 2A) as heterogeneous catalyst display the dense surface with heterogeneous distribution of particle and irregular shapes of particle sizes. However, the SEM images of the CaO catalyst doped with 5, 10, and 15 wt% Ba and carried out by calcination step at 900 °C for 4 h are illustrated in Figure 2B-D. It was noticeably observed that the morphology of the catalyst was changed from irregular shapes into spherical shapes, which smaller particles size than calcium oxide. It possibly resulted from the deposition of barium species into CaO framework during the synthesis catalyst. Calcined catalysts from waste egg shells causes an increase surface area, leading to better catalytic performance.

The actual elements of catalyst (15 wt% Ba/CaO) were investigated with energy dispersive X-ray spectroscopy

Table 1. Chemical compositions of calcined waste egg shell.

Compound	Concentration (wt %)
CaO	88.29
MgO	0.95
SiO ₂	0.05
P ₂ O ₅	0.43
SO ₃	0.23
SrO	0.07
Organic compound	9.98

Determined by XRF.

(SEM-EDS), and the result is shown in Figure 3. It was exhibited that, the content of Ca, O, and Ba were formed. Table 2 determined EDS analysis of barium doped on CaO. It was clearly seen that for 5 wt% Ba/CaO. The amount of Ca and Ba were 51.34 wt% and 1.78 wt%, respectively. For 10 wt% Ba supported on CaO, the actual elements of Ca and Ba were 54.77 wt% and 2.47 wt%, while 15 wt% Ba/CaO catalyst, the contents of Ca and Ba were 48.65 wt% and 2.80 wt%, respectively.

Table 2. EDS analysis of Ba loaded on CaO.

Catalyst	Element	Concentration (wt %)
5 wt% Ba/CaO	Ca	51.34
	O	46.89
	Ba	1.78
10 wt% Ba/CaO	Ca	54.77
	O	42.76
	Ba	2.47
15 wt% Ba/CaO	Ca	48.65
	O	48.55
	Ba	2.80

Measured by SEM-EDS.

Figure 1. FTIR spectra of neat CaO derived from egg shells.

Figure 2. SEM photograph of (A) neat CaO, (B) 5 wt% Ba/CaO, (C) 10 wt% Ba/CaO, and (D) 15 wt% Ba/CaO. The scale bars for panels are 50 μm.

3.2 Effect of Barium loading

Figure 4 shows the FAME contents from the transesterification via microwave irradiation of canola oil with methanol and the results obtained from four different heterogeneous catalysts (3 wt% catalysts). As can be seen, the methyl ester compositions in the reaction using neat CaO catalyst exhibited 89.52% conversion since it has sufficiently strong basic strength. The FAME conversion of 5 wt% Ba loading on egg shells derived CaO was 90.74 wt%. However, when the barium doping is increased up to 10 and 15 wt%, the FAME conversion slightly increased were 94.33% and 97.68 wt%, respectively. According to the biodiesel yield comparison, it could be noted that Ba doped base catalyst well distributed on CaO phase which might have the total number of available active catalytic sites from Ba-CaO catalyst increased. It was reported that the FAME yield significantly increased when the barium loading was increased due to barium may have improved the amount of basic sites of CaO.

Figure 3. SEM-EDS photograph of 15 wt%Ba/CaO.

Figure 4. Effect of catalyst concentration (5, 10, and 15 wt% Ba/CaO) on yield of FAME.

4 Conclusions

The present work show that the calcined of waste egg shells at 900 °C for 2 h are suitable catalyst for production of biodiesel via transesterification with microwave irradiation of 9:1 methanol: oil molar ratio. The calcined of waste egg shells consist mainly of CaO more than 88 wt% conversion to FAME, which can be considered heterogeneous catalyst for biodiesel production. Moreover, the 15 wt% Ba/CaO catalyst gave the highest catalytic performance of biodiesel synthesis, which yielded of FAME conversion, was 99.68% due to the catalyst had excellent activity and stability during transesterification reaction. CaO derived from waste egg shells can be utilized as economical and reduce waste disposal problem.

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