Biodiesel Production Via Ethanolysis Catalyzed by CaO Derived from Eggshell as Low-Cost Basic Heterogeneous Catalyst

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Abstract

Calcium oxide (CaO) derived from eggshell was applied as green and low-cost heterogeneous catalyst for the transesterification of palm oil with ethanol. The eggshell material was calcined in a furnace at designated temperature of 800 °C in air for 3 h to generate CaO materials. The obtained catalyst was characterized by TG–DTA, XRD, FT-IR, SEM, XRF, BET, TPD-CO_2 and Hammett indicator method. The ethanolysis of palm oil catalyzed by the obtained CaO was optimized in the term of reaction conditions; catalyst loading amount 13 wt.%, reaction temperature of 75±2 °C, ethanol/oil molar ratio of 12 : 1 and reaction time of 10 h; 97.5% yield of FAEE could be achieved in 10 h. The effects of adding a co-solvent on kinetic of the reaction and %FAEE yield was investigated. The results showed that eggshell is very cheap raw material for preparation of CaO catalyst to decrease biodiesel production cost and applications in the industrial scale.

KEYWORDS: CaO; Eggshell; Biodiesel; Ethanolysis; Fatty acid ethyl ester (FAEE); Ethanol

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Introduction

Generally, biodiesel is produced through transesterification reaction of long chain fatty acid alkyl esters (triglyceride) of oils or fat with a short chain alcohol, usually methanol (biodiesel product is fatty acid methyl ester (FAME)) or ethanol (biodiesel product is fatty acid ethyl ester (FAEE)) in the presence of a catalyst [1 – 4]. In the last decade, biodiesel production industrial scale utilizes methanol as a major reagent for the transesterification reaction because they give high biodiesel yield (FAME) under mild reaction condition and short reaction time due to its suitable physicochemical properties. However, the use of methanol for biodiesel production is not completely renewable because methanol derived from fossil sources (e.g. petroleum and coal) [5]. In addition, methanol is not only a highly toxic chemical, but also highly leaching of catalyst which would be contaminated in biodiesel product [6]. On the other hand, in the synthesis of biodiesel using ethanol as a reagent have many advantages as it is produced from biomass (e.g., sugars, corn syrup and starch) which is a renewable resource, less toxicity than methanol, the obtained FAEE more biodegradable, higher cetane number and heating value but lower cloud and pour points than that of FAME [5 – 7].

Nevertheless, several literature reported on biodiesel production using ethanol is difficult compared to the methanol due to the formation of stable emulsion during ethanolysis process and the lesser reactivity of ethanol than methanol [7]. Some works reported that the ethanolysis reaction using heterogeneous catalyst is limited to produce biodiesel. Li et al. [9] presented the use of mixed oxide catalysts derived from Mg-Co-Al-La as a heterogeneous catalyst in the biodiesel production of canola oil with ethanol showed FAEE yield 97% at the conditions of 200 °C, 25 atmospheric

pressure, ethanol:oil molar ratios of 14:1, catalyst 2 wt.% and time 5 h. Soldi et al. [10] used ion-exchange resin-sulfonated polystyrene as a catalyst for transesterification of soybean oil and beef tallow with ethanol to biodiesel. At the conditions of an ethanol to oil molar ratio of 100:1, 20 mol% of catalyst, 18 h and 64.8 °C led to 85 and 75% ethyl esters conversion in the case of soybean oil and beef tallow, respectively. Due to the ethanol has less reactivity than methanol and phase separation between hydrophilic ethanol, hydrophobic oil and solid catalyst, thus, the reaction often need high reaction temperature and pressure, long reaction time, higher amount of catalyst and ethanol to oil molar ratio [6, 11]. An important focus in this present work is to study the biodiesel production via ethanolysis catalyzed by CaO derived from eggshell as green and economical basic heterogeneous catalyst at the mild reaction condition. The effects of co-solvent on biodiesel yield and the optimum condition of the reaction were investigated.

Materials and Methods

Fig. 1 demonstrates a flow diagram of the experiments of this work. Then, the dried eggshell was crushed, sieved and calcined in a furnace at designated temperature of 800 °C in air for 3 h (refer to TG/DTA results) to generate CaO material. The obtained CaO material was characterized by X-ray powder diffraction (XRD), X-ray fluorescence (XRF) spectrophotometer, Scanning electron microscopy (SEM), Fourier Transforms Infrared (FT-IR) and Thermo-Gravimetric thermal analyzer (TG-DTA). Physicochemical properties of the obtained CaO material was analyzed by temperature programmed desorption (TPD), Hammett indicator method to evaluated the basic strength and Brunauer Emmett Teller (BET) to tested surface area.

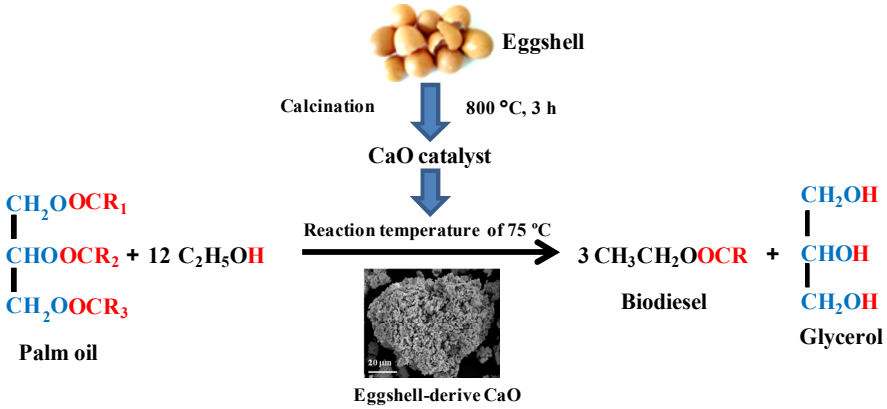

Fig. 1 Flow diagram of the experiments for biodiesel synthesis by ethanolysis using CaO obtained from eggshell.

The ethanolysis of palm oil was carried out in a three-neck round bottom batch reactor equipped a thermocouple. The mixture of CaO catalyst and ethanol was heated at 75±2 °C for 30 min and then added to palm oil of 50 mL. The reaction was operated with various catalysts loading amount of 5 – 15 wt.% relative to oil weight and the ratio of co-solvent to ethanol (%v/v) was set at 10 – 20%. To monitor the reaction, the solution mixture of 0.5 mL was sampled every 1 h for 12 h to analyze biodiesel yield in term of the fatty acid ethyl ester yield (%FAEE) by using proton nuclear magnetic resonance (^{1}H NMR) [6, 10]

Results and Discussion

Catalyst characterization

As forecasted, XRF results indicated that the obtained CaO material from calcined eggshell was composed mainly of CaO as 98.8 wt.% and approximately 1.2 wt.% of other oxides. Fig. 2 (a) demonstrates TG/DTA analysis of eggshell and the results were indicated that water molecules and

organic compounds showed weight loss in the range of 40 – 600 °C. The major weight loss due to the removal of CO_2 from decomposition of $CaCO_3$ to generate CaO species is appeared at around 600 – 800 °C and above 800 °C weight of the sample is invariable [12]. Based on TG/DTA results, the calcination eggshell at 800 °C for 3 h was chosen as a suitable condition for CaO catalyst generation. XRD patterns of calcined eggshell at 800 °C for 3 h shown in Fig. 2 (b) indicated that the peaks match with a crystalline phase of CaO as a major phase [12–13]. Furthermore, FT-IR spectra of calcined eggshell shown in Fig 2 (c) displayed a spectrum which reveals only a band of Ca-O stretching at 523 cm^{-1} and a very small hydroxyl group stretching at 3640 cm^{-1}. These results confirmed that eggshell after calcination at 800 °C for 3 h was completely transformed to CaO.

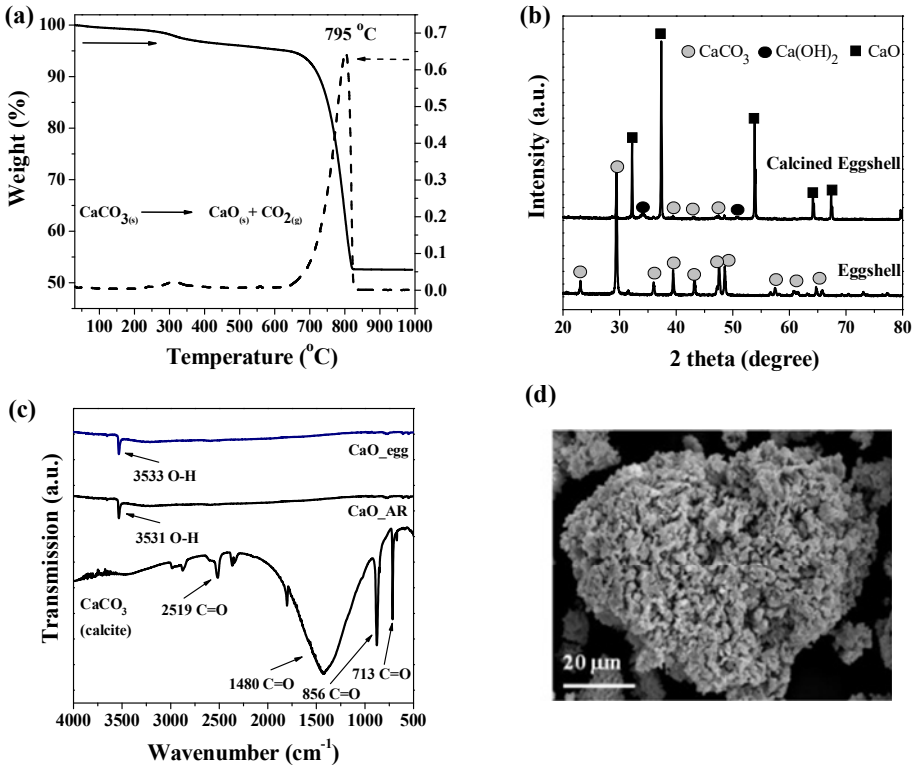

Fig. 2 (a) TG/DTA thermograms of eggshell, (b) XRD patterns and (c) IR spectra of eggshell and eggshell calcined at 800 °C for 3 h and (d) SEM images of the eggshell calcined at 800 °C for 3 h.

The morphology of the obtained CaO was probed by SEM as illustrated in Fig 2 (d). The SEM images of eggshell calcined at 800 °C for 3 h displays large particles with high porosity. The BET surface area of CaO catalyst derived from eggshell had 2.8 $m^2\ g^{-1}$ and the total basic site evaluated by CO_2-TPD which showed high total basic site of 215.5 µmol g^{-1}. In addition, the basic strength ($H_$value) of CaO derived from calcined eggshell tested by Hammett indicator method was in the rage of 15.0 – 18.4. These results suggest that higher surface area usually results in higher basic sites and basic strength which correlated to the catalytic activity of catalyst.

Optimization of reaction condition on the ethanolysis palm oil

Fig. 3 and Fig. 4 showed comparison of the effects of reagent between methanol and ethanol on biodiesel product and kinetics of reaction. The result indicated that eggshell-derived CaO catalyst showed very high activity and provides FAME yield of 92.2 % after only 3 h which using methanol as a reagent and the rate constant of the reaction (k) was 5.87×10^{-1} h^{-1}. On the other

hand, the use ethanol as a reagent showed slow rate of the reaction which gave only 72.2% FAEE and k value of 5.08×10^{-2} h^{-1}. These results described that nature of the reactants and reagent is one of the most factors affecting reaction rate. In general, methanol is smaller molecule and more reactive than ethanol because methanol can be converted to alkoxide anion ($R\text{-}O^{-}$) as a nucleophilic specie easier than ethanol when used the basic catalyst. The nucleophilic $R\text{-}O^{-}$ attacks electrophilic carbonyl carbon in triglyceride to produce biodiesel product and glycerol by-product [12].

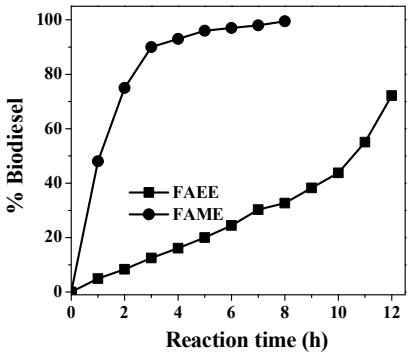

Fig. 3 Comparison of the effects of reagent between methanol and ethanol on biodiesel product.

The effect of co-solvent on ethanolysis reaction of palm oil to synthesize biodiesel was presented in Fig. 5 (a). Phase separation between hydrophilic ethanol (polar reagent), hydrophobic oil (non-polar substrate) and CaO as a solid catalyst is one of the major problem on the biodiesel production process. Addition of co-solvent into ethanol can enhance the reaction due to the mixing between ethanol and palm oil will be improving [12]. The result found that adding of 10 % v/v of acetone and THF gave %FAEE yield at the reaction time of 12 h to 94 % and 84 % respectively while non co-solvent system gives %FAEE yield only 72%. The k value of 10% v/v of acetone and THF were 1.25×10^{-1} h^{-1} and 8.31×10^{-2} h^{-1} respectively which higher than k value of non co-solvent system (5.08×10^{-2} h^{-1}).

Fig. 5 (b) demonstrated the effects of catalyst loading amount on biodiesel product. The optimal catalyst loading was tested by varying the CaO catalyst obtained from calcined eggshell from 5 wt.% to 15 wt.%. The result showed that %FAEE yield increased when catalyst loading amount was increased from 5 wt.% to 13 wt.%. Biodiesel yield was 97.5% in 10 h with 13 wt.% loading amount of catalyst. Generally, CaO catalyst generates ethoxide anion from ethanol as a nucleophile and then they attack electrophile carbonyl carbon in triglyceride to produce biodiesel [3, 13]. As a result, increasing CaO catalyst will generally improve the biodiesel product. However, %FAEE did not increase when catalyst loading amount more than 13 wt.% because of the limitation of mass transfer of reactants to the catalyst and phase mixing of the mixture (palm oil, ethanol and CaO catalyst) as high viscosity of slurry.

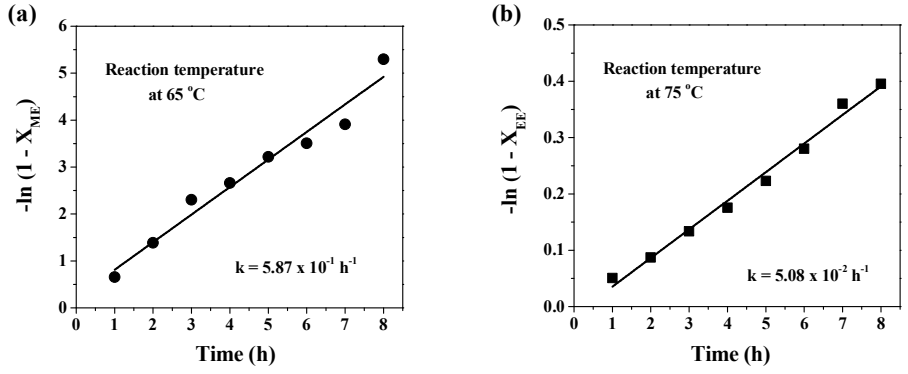

Fig. 4 (a) and (b) kinetics study of reaction. Reaction condition: catalyst amount of 5 wt.%, alcohol/oil molar ratio of 12:1, reaction temperature of 65±2 °C using methanol and 75±2 °C using ethanol.

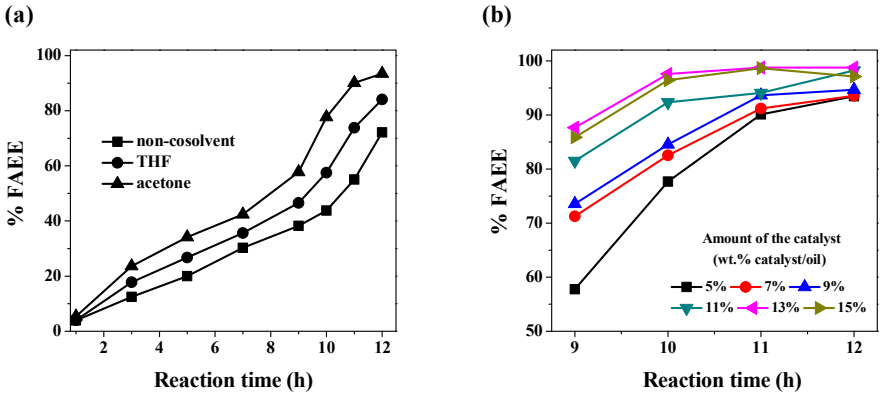

Fig. 5 (a) %FAEE of with and without % v/v of co-solvent systems; reaction condition: catalyst amount of 5 wt.% , ethanol/oil molar ratio of 12:1 and reaction temperature of 75±2 °C. (b) Effect of catalyst loading amount of % FAEE yield; reaction condition: 10% v/v acetone as a co-solvent system, ethanol/oil molar ratio of 12:1 and reaction temperature of 75±2 °C.

Conclusion

The results obtained in this work showed that eggshell-derived CaO catalyst for biodiesel production via ethanolysis reaction could be achieved %FAEE 97.5% in 10 h under the optimal reaction conditions of catalyst amount of 13 wt.%, ethanol to palm oil molar ratio of 12:1, reaction temperature of 75±2 °C and 10% v/v of acetone as a co-solvent system. The kinetics data were evaluated to compare methanolysis with ethanolysis reaction and the effect of with and without co-solvent system on biodiesel yield. All of the results indicated that eggshell-derived CaO catalyst and co-solvent system are high potential for improving biodiesel production process with ethanolysis reaction which was green and low-cost method.

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