The Optimized Conditions of Ethanolysis Reaction of Palm Oil to Biodiesel Product Using Eggshells-Derived CaO as a Solid Heterogeneous Catalyst

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Received 13 August 2018; Revised 17 August 2018; Accepted 21 August 2018

Abstract

Eggshells were used as raw material to generate CaO as a solid heterogeneous catalyst for biodiesel production via ethanolysis of palm oil. The catalysts derived from eggshells at 800°C provided high activity which high yield of fatty acid ethyl ester (FAEE) of 97.53% was obtained from the optimum conditions. After treatment process, the high quality of biodiesel product was obtained and passed all significant fuel properties of the ASTM and EN standards. These results could be suggested that waste eggshells showed good potential to be used as catalyst for biodiesel production with ethanol reagent.

KEYWORDS: Kinetics; Optimization reaction; Ethanolysis; Eggshells; Biodiesel product

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Introduction

Biodiesel is one of the best candidates for a petroleum diesel oil substitute in any diesel-engine without the need for modification because its fuel properties is close to petroleum diesel such as kinematic viscosity, cloud point, pour point, copper strip corrosion and oxidation stability [1]. In addition, it is clean, non-toxic, lower polluting emission gases (e.g. CO, NO_x, and SO_x), biodegradable, and inexpensive [2]. Moreover, biodiesel is also produced from many kind of oils for example palm oil, jatropha oil, soybean oil, rubber seed oil, sun flower oil and animal fat which were obtained from agricultural raw materials as a high potential oil feedstock for biodiesel production [3].

Generally, biodiesel can be produced from any raw material as a triglyceride via transesterification reaction which reacted with short chain alcohol namely methanol to generate fatty acid methyl ester (FAME) [2, 4]. Although, the industrial scale mostly utilized methanol as a reagent for biodiesel production, there were many problems for example toxicity, highly leaching of catalyst and price volatility based on petroleum fuel [5]. Consequently, the use of ethanol as a reagent instead of methanol is the interesting choice to produce biodiesel product (fatty acid ethyl ester; FAEE) especially in Thailand where there are a lot of biomass raw materials for ethanol production such as cane, corn, rice and cassava.

Recently, we have reported on the biodiesel production via ethanolysis catalyzed by CaO derived from eggshell as low-cost basic heterogeneous catalyst [5]. The results found that eggshell-derived CaO as a catalyst was high performance to catalyze the ethanolysis reaction of palm oil. The reaction conditions of catalyst loading amount 13 wt.%, reaction temperature of 75 (±2) °C, ethanol to palm oil molar ratio of 12 : 1 and reaction time of 10 h, could be generated biodiesel as a FAEE of 97.5%. Nevertheless, the optimum condition of reaction and fuel properties of the obtained biodiesel product were not reported. Therefore, the aim of this work was to study the optimization reaction of palm oil through ethanolysis using eggshells-derived CaO as a heterogeneous catalyst to produce biodiesel product. Furthermore, quality assessment of the obtained final biodiesel product was also investigated, discussed and compared with biodiesel obtained from methanolysis reaction.

Materials and Methods

The methanol (CH_3OH) 95.0% purity, ethanol (C_2H_5OH) 95.0% purity, hexane (C_6H_{14}) 95.0% purity, acetone (C_3H_6O) 95% and potassium hydroxide (KOH) 99.0% purity were purchased from Fluka and Acros Chemical Co. Ltd. Palm olein oil with free fatty acid (FFAs) amount of 0.29 mg KOH/g of oil was purchased from commercial sources in Thai market. The collected eggshells were obtained from local restaurants, washed with water, dried, grinded and calcined in a furnace at 800 °C for 3 h [5 – 7]. After that, the obtained CaO powder was characterized by X-ray powder diffraction Cu Kα1 radiation, λ = 0.1541 nm (XRD-6100 Shimadzu, Japan)

The ethanolysis reactions were carried out in a 250 mL three-neck round-bottom flask equipped with a reflux condenser and thermometer. The reaction started by mixing ethanol and CaO catalyst of 13%.wt (refer to report from Roschat et al. [5]) at 75 ±2 °C and then a preheated of palm oil was added (50 mL). In the end of reaction, the mixture was separated by filtration method and then the excessive amount of ethanol was heated to eliminate. Finally, the obtained product was separated between biodiesel as a major product and glycerol as a minor product by a separatory funnel.

The final biodiesel product was purified by extraction method with hexane. In order to eliminate the hexane solvent, the rotary evaporator was used in this step. The conversion of palm oil to biodiesel product was evaluated by proton nuclear magnetic resonance (^{1}H-NMR) on a Brüker AscendTM 500 MHz as depicted in Fig. 1 [5, 8]. To determine fuel properties of the final biodiesel product, it was tested for standard fuel properties followed the American Society for Testing and Material methods (ASTM-D6751) and European standard (EN-14214) namely kinematic viscosity, acid number, oxidation stability, ester content, calcium content, heating value and sulfated ash.

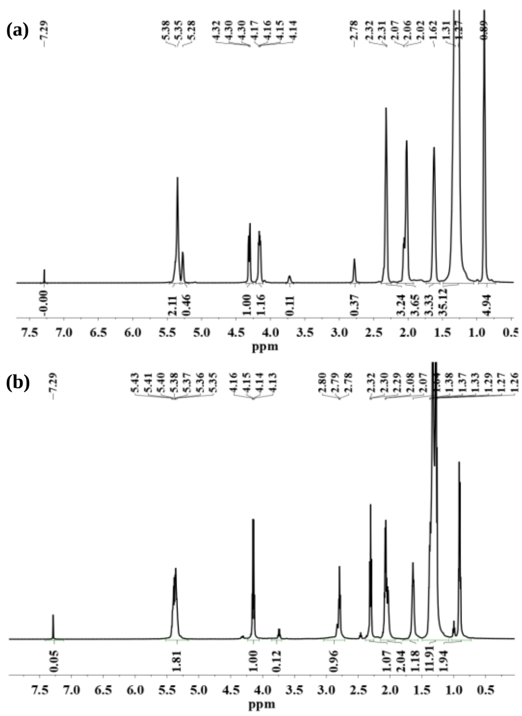

Fig. 1 Analysis of biodiesel produced from the ethanolysis of palm oil by ^{1}H-NMR; (a) palm oil as raw material and (b) biodiesel product (FAEE).

Results and Discussion

XRD pattern of CaO derived from calcination eggshells revealed that major component was CaO phase because the peak matched each other at around 2θ of 32º, 37º, 53º, 64º and 67º according reference number as PDF No. 00-048-1467 as shown in Fig. 2. In addition, a minor phase as a $Ca(OH)_2$ were observed due to the reaction of CaO material reacted with moisture. These results were also similar with the obtained reports of Roschat et al. [5, 9], Viriya-empikul et al. [6] and Muhammad et al. [10]. Therefore, these results indicated that the calcination eggshells at 800 °C for 3 h can be completely converted $CaCO_3$ phase of eggshells to CaO phase.

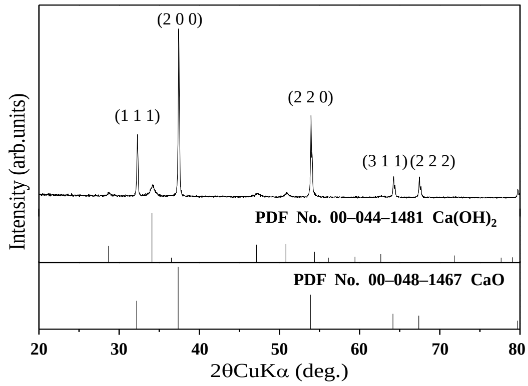

Fig. 2 XRD diffractogram of CaO derived from calcination eggshells at 800 °C for 3 h.

Conversion of palm olein oil to biodiesel product by ethanolysis in this work was studied with various amount of co-solvent (acetone) in ethanol 5 – 15% v/v, ethanol to oil molar ratios of 12:1 – 21:1 and reaction time of 5 – 10 h, respectively. As shown in Fig. 3, addition of 10% v/v of acetone in ethanol resulted higher percentage yield of FAEE when compared with addition of acetone 5% v/v and 15% v/v. This data was generally to know that the addition of co-solvent in the biodiesel production can improve to shift the equilibrium reaction towards the direction of biodiesel formation because the reaction mixture between ethanol (hydrophilic) and palm olein oil (hydrophobic) can be mixed progressively [11, 12]. Nevertheless, the exceeding acetone as a co-solvent may be decreased biodiesel yield due to glycerol by-product can be dissolved very well both acetone and ethanol and its will be inhibited the reaction. Thus, 10% v/v of acetone as a co-solvent was selected to be optimum condition for ethanolysis reaction.

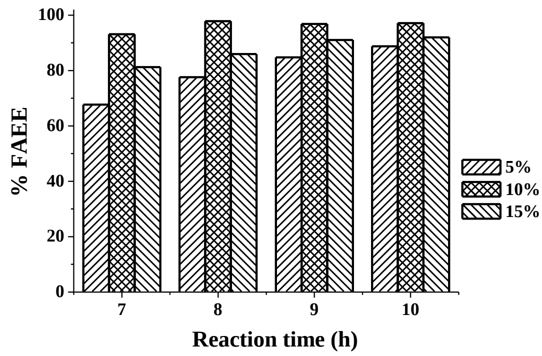

Fig. 3 The effect of amount of acetone as a co-solvent on FAEE yield; reaction condition: catalyst amount of 13 wt.%, ethanol/oil molar ratio of 12:1 and reaction temperature of 75 ± 2 °C.

Fig. 4 demonstrated the effect of ethanol to oil molar ratio on FAEE yield at fixed variable condition of catalyst loading amount of 13 wt.%, 10% v/v acetone as a co-solvent system, reaction temperature of 75 ± 2 °C and reaction time for 8 h. The result was observed that the %FAEE yield slightly increased when the ethanol to oil molar ratio was increased from 12:1 to 15:1. However, the ethanol to palm oil molar ratio beyond 15:1, %FAEE yield gradually decreased due to the exceeding amount of ethanol would dissolve glycerol as a by-product to make emulsifier and inhibit the reaction [9, 11]. Moreover, the ethanolysis reaction may be reversible which was affected on the rate constant of the reaction (k). Hence, the molar ratio of ethanol to oil as 15:1 was sufficient to optimize the reaction.

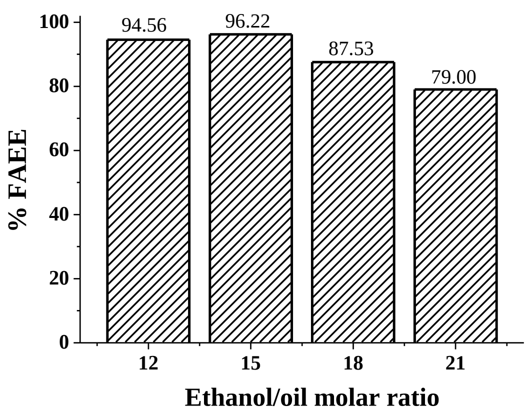

Fig. 4 Effects of ethanol to oil molar ratio on %FAEE yield; reaction conditions: catalyst amount of 13 wt.%, 10% v/v acetone as a co-solvent system, reaction temperature of 75 ± 2 °C and reaction time for 8 h.

Reaction time is one of the most important parameters for biodiesel production because it directly affected on the cost production both energy consumption and the reaction rate. Fig. 5 displayed the effect of reaction time on the percentage of biodiesel yield in the reaction process. In this case, the ethanolysis of palm oil to generate biodiesel product required the sufficient reaction time for 6 h. The FAEE yield dramatically increased from the reaction time 4 h to 6 h, after reaction time 6 h the biodiesel yield gradually decreased. This phenomenon can be described that the biodiesel product may be transformed emulsion or soap during the reaction of catalyst and fatty acid.

Table 1 the comparison between biodiesel from methanolysis reaction (FAME) against ethanolysis reaction (FAEE).

Fuel properties	Standard biodiesel	FAME[a]	FAEE[b]
Kinematic viscosity @40°C (cSt)	3.50-5.00	4.44	4.92
Acid number (mg KOH/g oil)	< 0.50	0.29	0.31
Ester content (%)	> 96.50	96.72	97.53
Oxidation Stability (h)	> 6	14.6	16.2
Sulfated ash (%w/w of oil)	≤ 0.02	≤0.01	≤0.01
Calcium content (mg/kg (ppm))	5	≤3	≤3
Heating value (kcal/kg)	–	9512	9987

[a] Reaction conditions: amount of catalyst loading 5 wt.%, methanol/oil molar ratio of 15:1 and reaction temperature of 65 ± 2 °C and time of 4 h.

[b] Reaction conditions: amount of catalyst loading 13 wt.%, 10% v/v acetone as a co-solvent system, ethanol/oil molar ratio of 15:1 and reaction temperature of 75 ± 2 °C and time of 6 h.

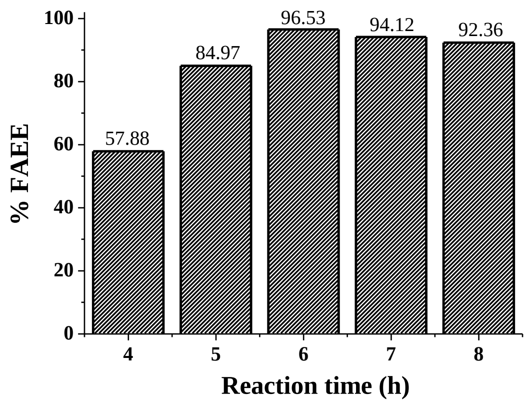

Fig. 5 Effect of reaction time on %FAEE yield; reaction conditions: amount of catalyst loading 13 wt.%, 10% v/v acetone as a co-solvent system, ethanol/oil molar ratio of 15:1 and reaction temperature of 75 ± 2 °C.

Fuel properties of the obtained biodiesel product after purification by extraction method with hexane were evaluated according to the ASTM-D6751 and EN-14214 such as kinematic viscosity, acid number, oxidation stability and ester content which were the important properties of bio-auto fuels for diesel-engine [13, 14]. This result showed that the final biodiesel product has qualified to meet within limits set by various standards for bio-auto fuels as presented in Table 1.

Conclusion

A significant finding in this work was optimum reaction condition as a catalyst loading amount of 13 %.wt, ethanol to oil molar ratio of 15:1, amount of acetone as co-solvent system of 10% v/v, reaction temperature of 75 ± 2 °C and reaction time for 6 h which could be achieved biodiesel product with a FAEE yield over 97%. Additionally, after purification the final biodiesel product using extraction with hexane, the obtained high quality biodiesel was according all the ASTM and EN standard specifications properties of bio-auto fuels for diesel-engine. Therefore, the CaO derived from eggshells as a solid heterogeneous catalyst for ethanolysis of palm oil to produce biodiesel product should be extremely promoted and suggested for applications as green and low-cost in industrial biodiesel production.

Acknowledgements

The authors were extremely grateful to the Program of Chemistry, Faculty of Science and Technology, Biomass Energy Research Laboratory under Center of Excellence on Alternative Energy and Research and Development Institute, Sakon Nakhon Rajabhat University-Thailand, for providing the equipment and tools for experimentation. The authors would also thankful the financial support from Sakon Nakhon Rajabhat University for this research by the fiscal year 2018 (Contract No. 26/2561 and 5/2561).

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