



Catalytic performance enhancement of CaO by hydration-dehydration process for biodiesel production at room temperature

Wuttichai Roschat^{a,b,*}, Sunti Phewphong^b, Amonrat Thangthong^c, Preecha Moonsin^d, Boonyawan Yoosuk^e, Teadkai Kaewpuang^f, Vinich Promarak^f

^a Program of Chemistry, Faculty of Science and Technology, Sakon Nakhon Rajabhat University, Mueang District, Sakon Nakhon 47000, Thailand

^b Biomass Energy Research Laboratory, Center of Excellence on Alternative Energy, Research and Development Institute, Sakon Nakhon Rajabhat University, Mueang District, Sakon Nakhon 47000, Thailand

^c Program of Environment Science, Faculty of Science and Technology, Sakon Nakhon Rajabhat University, Mueang District, Sakon Nakhon 47000, Thailand

^d Program of Chemistry, Faculty of Science, Ubon Ratchathani Rajabhat University, Mueang District, Ubon Ratchathani 34000, Thailand

^e National Metal and Materials Technology Center (MTEC), 114 Thailand Science Park, Phahonyothin Road, Klong 1, Klong Luang, Prathumthani 12120, Thailand

^f Department of Materials Science and Engineering, School of Molecular Science & Engineering, Vidyasirimedhi Institute of Science and Technology, Wangchan, Rayong 21210, Thailand



ARTICLE INFO

Keywords:

Biodiesel
Calcium oxide
Hydration-dehydration process
Room temperature
Transesterification

ABSTRACT

This research presents an efficient technique to enhance the catalytic activity, surface area and total basicity of CaO with hydration-dehydration process to be the catalyst for the transesterification of palm oil to biodiesel. The catalytic performance of the resulted catalyst was tested via transesterification reaction of palm oil at room temperature ($30 \pm 2^\circ\text{C}$) and was compared against commercial CaO and CaO derived from natural calcium carbonate sources. Under the optimal reaction conditions (catalyst loading of 5 wt%, methanol to oil molar ratio 12:1), FAME yields were approximately 94% for CaO_{HY} and 60.5%, 55.3%, 49.5% and 51.4% for CaO_{com}, CaO_{egg}, CaO_{gol} and CaO_{riv} as catalysts, respectively. Catalyst reusability and scaling up of biodiesel production from 50 mL to 1.5 L were also investigated. The obtained biodiesel product after purification and treatment process showed high quality fuel properties within the range of biodiesel standard and similar with high-speed diesel. Furthermore, the used CaO_{HY} as a solid heterogeneous catalyst at room temperature was not only low-cost but also environmentally-friendly, showing a high potential in the biodiesel production.

1. Introduction

Biodiesel is a candidate alternative liquid fuel to substitute petroleum diesel because its fuel properties is close to petroleum diesel and can be used on its own or mixed with petroleum diesel in any diesel engines without major modifications of the engines [1–2]. It is also non-toxic, biodegradable with low smoke emission (mainly composed of particulate matter (PM), carbon dioxide (CO₂), carbon monoxide (CO), sulfur oxide (SO_x) and nitrogen oxides (NO_x) [2–5]). Biodiesel is generally known as mono alkyl esters of long chain fatty acid which can be produced from vegetable oil (e.g. palm oil, soy bean oil, jatropha oil and rubber seed oil), animal fat and waste cooking oil via a direct transesterification reaction with small molecule alcohol (methanol or ethanol) in the presence of a catalyst [5–8].

Generally, KOH and NaOH are widely used as homogeneous catalysts for biodiesel production in the industrial scale due to their excellent catalytic activity and high yield of biodiesel product under mild

reaction conditions and short reaction time [9,10]. Nevertheless, large amount of water is required to eliminate these catalysts out of biodiesel product after reaction is completed. Furthermore, these catalysts are highly sensitive to water and free fatty acids in the oil which is the main cause of the soap formation and reduction of biodiesel yield. Such disadvantages of homogeneous catalyst lead to the increased cost of biodiesel production and environmental impact [5,10,11]. In contrast, heterogeneous solid base catalysts are promising for solving the drawbacks of homogeneous catalysts because they are easy to be separated from the reaction mixture and can be reused for several times. They are also less sensitive to the presence of water and free fatty acid in the oil and require no further cleaning of the biodiesel product [1,5,12].

Among the heterogeneous catalysts, calcium oxide (CaO) is one of the most excellent materials as green solid base catalyst for biodiesel synthesis due to its environmental friendliness, non-toxicity, low cost, good catalytic activity and low solubility in methanol [10,13]. Additionally, CaO can be derived from natural materials such as hydrated

* Corresponding author at: Program of Chemistry, Faculty of Science and Technology, Sakon Nakhon Rajabhat University, Mueang District, Sakon Nakhon 47000, Thailand.
E-mail address: roschat1@gmail.com (W. Roschat).

lime [5], river snail shells [10], sea shells [9], chicken manure [12], bivalve clam shells [13], egg shells [14] and mussel shells [15]. Although many authors have reported successful transesterification reaction catalyzed by CaO, the reaction rate was slow and thus required a longer reaction time of at least 3–8 h (reaction temperature of 60–65 °C) to complete and a higher amount of catalyst and methanol. These requirements directly resulted in high biodiesel production costs [16–18]. All the reports on waste material derived CaO catalysts show lower surface area and basicity which is generally known to be the major problem in heterogeneous reaction [5,18]. Consequently, decreasing of reaction time, amount of catalyst, methanol to oil molar ratio and reaction temperature need to be considered to reduce the biodiesel production cost, especially in the industrial scale.

Recently, several articles reported the improvement of catalytic activity of CaO with hydration-dehydration technique in the transesterification of oil (palm oil and waste frying oil) with methanol. Yoosuk et al. [18] found that the decomposed-hydrated CaO exhibits higher catalytic activity than CaO generated from direct calcination of CaCO₃. Under mild reaction conditions and short reaction time, 93.9% yield of biodiesel was observed (molar ratio of 15:1 methanol/oil, catalyst weight of 7 wt%, reaction temperature of 60 °C and time of 1 h). Asikin-Mijan et al. [16] showed that hydration treated clamshell derived CaO could convert palm oil to biodiesel with approximately 98% yield after 2 h of reaction time with molar ratio of 9:1 methanol/oil, catalyst amount of 1 wt%, and temperature of 65 °C. The similar results were also obtained by Niju et al. [13,14]. They reported that the calcination hydration processed egg shell and white bivalve clam shell showed high activity and provided biodiesel yield of around 94 wt% under 5 wt% of egg shell derived catalyst and 7 wt% of white bivalve clam shell derived catalyst with the same molar ratio of 12:1 methanol to oil, reaction temperature of 65 °C and reaction time of 1 h.

Thus, an important focus of this work is to study the preparation, characterization and catalytic activity of CaO resulted from calcination–hydration–dehydration process whose activity, basicity, and surface area are improved during the process. In addition, the present work also focuses on its effects on transesterification reaction of palm oil to biodiesel product at room temperature, compared with the effects of commercial CaO and CaO derived from waste shell materials such as eggshells, river snail shells and golden apple snail shells. Several parameters, such as catalyst loading amount, methanol to oil molar ratio, reusability of catalyst and scaling up of transesterification reaction were investigated. Furthermore, fuel properties of the obtained biodiesel product after purification and treatment process were evaluated by using European Standard methods (EN14214) and American Society for Testing and Material (ASTM) methods.

2. Materials and methods

2.1. Materials

Palm olein oil with free fatty acid (FFAs) amount of 0.28 mg KOH/g and water content of 0.011% w/w was purchased from Morakot Industries PCL., Thailand. Methanol (99.5%) and hexane (98%) were obtained from Fluka and calcium oxide commercial grade (denoted as CaO_{com}) was purchased from Acros Chemical Co. Ltd. Eggshells, river snail shells and golden apple snail shells were collected from local restaurants and they were washed with water, dried in an oven, grinded, sieved and calcined at 800 °C in air for 3 h with a heating rate of 10 °C/min to produce CaO (denoted as CaO_{egg}, CaO_{riv} and CaO_{gol} respectively) [9,10,19]. Hammett indicators (phenolphthalein, thymolphthalein, indigo carmine, 2,4-dinitroaniline, and 4-nitroaniline) used in this work were purchased from Aldrich and Fluka.

2.2. Catalyst preparation and characterization

Preparation diagram of enhancing catalytic performance of CaO by

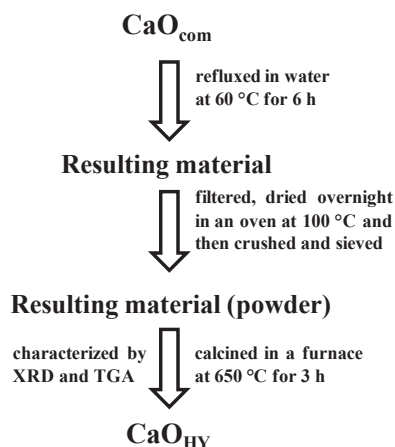


Fig. 1. Flow diagram of the CaO_{HY} catalyst preparation by hydration-dehydration-calcination process.

hydration–dehydration process (denoted as CaO_{HY}) are presented in Fig. 1. Firstly, CaO_{com} was refluxed in water at 60 °C for 6 h following the method of Yoosuk et al. [18]. After that, the resulted material was filtered, dried overnight in an oven at 100 °C and then crushed and sieved. Finally, the resulted materials were calcined in a furnace at 650 °C with a heating rate of 5 °C/min in air for 3 h (refer to TGA results) to generate CaO_{HY}.

The obtained CaO_{HY} powder was characterized by X-ray diffraction (XRD) method using a Brüker D5005 X-ray diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) at 1600 W, 40 kV and 40 mA, and 0.02° per step and the results are compared with CaO_{com}. JEOL JSM 6010LV Scanning Microscope was used to investigate the sample morphology at an accelerated voltage of 10 kV. Brunauer–Emmett–Teller (BET) plot was applied to study surface area with determined isotherm of low temperature adsorption and desorption of N₂ gas using He as carrier gas on a Bel-sorp-mini II (Bel-Japan). Basic site properties and basic strength of CaO_{HY} were tested by temperature programmed desorption method (TPD) using Chemisorption Analyzer (Belcat B) with CO₂ as an investigation molecule and Hammett indicator method. The CaO_{HY} was also analyzed by Fourier transforms infrared (FT-IR) spectroscopy using a Perkin–Elmer RXI spectrometer in the range of 400–4000 cm⁻¹ with resolution of 4 cm⁻¹ and potassium bromide (KBr) as a matrix.

2.3. Catalytic performance tests and product analysis

The transesterification of palm oil catalyzed by CaO_{HY} was carried out in a 250 mL three-neck round-bottom flask batch reactor equipped with a reflux condenser, a thermometer and a magnetic stirrer. CaO_{HY} and methanol were mixed at room temperature (30 ± 2 °C) with stirring rate of 500 rpm and then added to the oil of 50 mL. The transesterification reactions were performed with various catalysts loading amount (range of 1.0–7.0 wt%) corresponding to oil weight and methanol to oil molar ratios (range of 6:1–15:1). The effect of scaling up from 50 mL to 1.5 L of palm oil in the reaction was also studied.

To follow the reaction progress, 0.5–1.0 mL of reaction mixture was sampled every specific period of time and centrifuged to separate catalyst from the mixture. The excessive amount of methanol in the mixture was evaporated in an oven at 80 °C for 3 h before the analysis of biodiesel product in term of the fatty acid methyl ester (%FAME). The conversion of oil to biodiesel product was examined by proton nuclear magnetic resonance (¹H NMR) on a Brüker Ascend™ 500 MHz spectrometer using tetramethylsilane (TMS) and CDCl₃ as internal reference and solvent, respectively. The %FAME was calculated according to the following Eq. (1):

Download English Version:

<https://daneshyari.com/en/article/7158592>

Download Persian Version:

<https://daneshyari.com/article/7158592>

[Daneshyari.com](https://daneshyari.com)