



Economical and green biodiesel production process using river snail shells-derived heterogeneous catalyst and co-solvent method



Wuttichai Roschat^a, Theeranun Siritanon^a, Teadkai Kaewpuang^a, Boonyawan Yoosuk^b, Vinich Promarak^{c,*}

^a School of Chemistry, Institute of Science, Suranaree University of Technology, Muang District, Nakhon Ratchasima 30000, Thailand

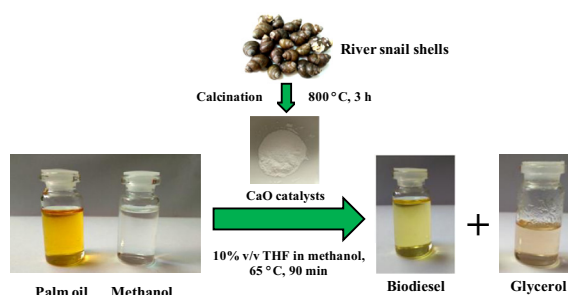
^b Renewable Energy Laboratory, National Metal and Materials Technology Center (MTEC), National Science and Technology Development Agency, 114 Thailand Science Park, Phahonyothin Road, Klong 1, Klong Luang, Pathumthani 12120, Thailand

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

HIGHLIGHTS

- River snail shells-derived CaO catalyst was synthesized for the first time.
- 98.5% FAME yield was achieved in 90 min under the use 10% v/v of THF in methanol.
- The transesterification reaction mechanism is experimentally demonstrated.
- The co-solvent method of THF/methanol successfully decreases activation energy of reaction.

GRAPHICAL ABSTRACT



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ABSTRACT

River snail shells-derived CaO was used as a heterogeneous catalyst to synthesize biodiesel via transesterification of palm oil with methanol. The shell materials were calcined in air at 600–1000 °C for 3 h. Physicochemical properties of the resulting catalysts were characterized by TGA–DTG, XRD, SEM, BET, XRF, FT-IR and TPD. CaO catalyzed transesterification mechanism of palm oil into biodiesel was verified. The effects of adding a co-solvent on kinetic of the reaction and %FAME yield were investigated. %FAME yield of 98.5 ± 1.5 was achieved under the optimal conditions of catalyst/oil ratio of 5 wt.%; methanol/oil molar ratio of 12:1; reaction temperature of 65 °C; 10% v/v of THF in methanol and reaction time of 90 min. The results ascertained that river snail shells is a novel raw material for preparation of CaO catalyst and the co-solvent method successfully decreases the reaction time and biodiesel production cost.

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1. Introduction

Biodiesel is known to be an alternative to diesel fuel derived from petroleum source. It can be used on its own or mixed with diesel in any diesel-engine vehicles. Advantages of biodiesel are biodegradability, non-toxicity, and lower CO₂ and sulfur emission

(Wang et al., 2015). Biodiesel is composed of long chain fatty acid alkyl esters typically produced from a reaction between a triglyceride in fats or oils and short chain alcohols, mainly methanol (Leung et al., 2010).

Generally, biodiesel production via transesterification reaction requires a catalyst to promote the reaction. Commonly, homogeneous catalysts such as KOH and NaOH are widely used because they give high biodiesel yield under mild reaction condition and short reaction time (Lee et al., 2015). However, the use of these catalysts has drawbacks as large amount of water is required to wash

* Corresponding author. Tel.: +66 33 014150; fax: +66 33 014445.

E-mail address: vinich.p@vistec.ac.th (V. Promarak).

the produced biodiesel to eliminate the catalyst and soaps. Homogeneous catalysts are also difficult to be reused and they can corrode reactors (Farooq et al., 2013). Such disadvantages increase the cost of biodiesel production. On the other hand, heterogeneous basic catalysts have many advantages as they are cheap, environmentally friendly and non-toxic. It is possible to reuse and recycle heterogeneous basic catalysts without employing water to clean the biodiesel product. Moreover, the reaction usually results in pure glycerol as a by-product (Farooq et al., 2013; Reyer et al., 2014).

Among the heterogeneous catalyst, calcium oxide (CaO) is one of the best heterogeneous catalysts with good catalytic activity and low solubility in methanol. It is also cheap, environmentally friendly, easy to prepare and it can be easily recovered and recycled (Witoon et al., 2014; Chen et al., 2014). Many research articles have reported the study of natural materials such as egg shells (Wei et al., 2009) and sea shells (Lee et al., 2015; Nakatani et al., 2009) as starting materials for CaO preparation via calcination process. It is obvious from literatures that different types of shells give CaO with different activity. Moreover, reactions catalyzed by shell-derived CaO usually take 3–6 h to finish which is still quite slow comparing to homogeneous catalyzed reactions (Boro et al., 2011). It is the focus of this work to study the preparation and catalytic activity of CaO catalysts prepared from river snail shells. A river snail is one kind of freshwater mussels in the family Viviparidae commonly found around muddy river area in Thailand. Their fleshy part is consumed and the shells are always wasted.

Another purpose of the current research is to present a strategy to accelerate the catalyzed reactions by a co-solvent method. The method has been applied to improve the transesterification process. For example, tetrahydrofuran (THF), acetone, diethyl ether and chlorobenzene were used as a co-solvent in homogeneous catalyzed biodiesel production (Alhassan et al., 2014; Thanh et al., 2013; Soriano et al., 2009; Luu et al., 2014a,b; Babaki et al., 2015). Some reports also show that the co-solvent method can reduce the reaction time and reaction temperature and improve some fuel properties of the produced biodiesel (Luu et al., 2014a,b; Alhassan et al., 2014).

In addition, the transesterification reaction with the prepared CaO is systematically studied in detail including the condition optimization, reaction mechanism and the reusability of the catalysts. The obtained knowledge is expected to deepen the understanding of the reaction itself and to be useful in real applications.

2. Methods

2.1. Materials

The palm oil (acid value = 0.30 mg KOH g⁻¹) and waste cooking oil (WCO, acid value = 1.54 mg KOH g⁻¹) in this work were purchased from commercial sources in Thai market. The fatty acid profile of the palm oil is presented in previous report (Roschat et al., 2016). River snail shells were collected from local restaurants. Methanol (99.5%), acetone (99%), 1-propanol (99%), 2-propanol (99%), tetrahydrofuran (THF 99.5%), ethanol (99%), and ethylene glycol (99%) were obtained from Fluka. Hammett indicators namely phenolphthalein, indigo carmine, 2,4-dinitroaniline and 4-nitroaniline of AR grade purchased from Aldrich and Fluka were used in this work.

2.2. Catalyst preparation and characterization

The river snail shells were washed with water several times and air-dried overnight in an oven at 100 °C. The dried river snail shells

were crushed, sieved and calcined at different temperatures (600–1000 °C) with a heating rate of 10 °C/min for 3 h.

The elemental compositions of river snail shells and the obtained catalysts were analyzed by a PHILIPS Magi X diffuse wavelength X-ray Fluorescence (XRF) spectrophotometer with 1 kW Rh K α radiation. Thermal decomposition of the shells was analyzed by a Rigaku TG/DTA 8120 thermal analyzer under air flow with a heating rate of 10 °C/min. Phases of both river snail shells and the resulting calcined materials was determined by a PHILIPS X'Pert-MDP X-ray diffractometer using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) at 1400 W, 40 kV and 40 mA. JEOL JSM 6010LV Scanning Microscope was used to investigate the samples. The samples were also analyzed by Fourier transforms infrared (FT-IR) spectroscopy using a Perkin-Elmer FT-IR spectroscopy spectrum RXI spectrometer.

Brunauer Emmett Teller (BET) was used to investigate surface area, mean pore diameter and pore volume based on adsorption and desorption isotherm of N₂ gas on the Bel-sorp-mini II (Bel-Japan). Basic strength and basic site properties of calcined river snail shells were evaluated by Hammett indicator method and temperature programmed desorption method (TPD) on the Chemisorption Analyzer (Belcat B) with CO₂ as the probe molecule (Chen et al., 2014).

2.3. Transesterification reaction

All transesterification reactions were carried out in a three-neck round bottom batch reactor equipped with a condenser and a thermocouple. The mixture of river snail shells-derived CaO catalysts and methanol was heated at 65 °C and added to palm oil. The reaction conditions were designed as follows: methanol to oil molar ratio of 6:1–18:1, amount of catalyst to oil is 1–7 wt.% and magnetic stirring speed of 300 rpm. Both the type and the amount of the co-solvent were varied. The ratio of co-solvent to methanol (%v/v) was set at 5% and 10%. After the reaction completed, the mixture was filtered to separate the solid catalyst. The catalysts were collected and reused for the next run.

To monitor the reaction, 0.5–1.0 mL of the reaction mixture was collected every 30 min for 10 h for analysis. Excess methanol and co-solvent in the sampled mixture were evaporated in an oven before the analysis of biodiesel yield in term of the fatty acid methyl ester yield (%FAME) was performed. Proton nuclear magnetic resonance (¹H NMR) on a Bruker Ascend™ 500 MHz spectrometer was employed to evaluate %FAME. Tetramethylsilane (TMS) and CDCl₃ were used as the internal reference and a solvent, respectively (Monteiro et al., 2009; Roschat et al., 2012, 2016). A representative example of ¹H NMR spectra and their interpretation are presented in the Supporting Information (Fig. S1).

2.4. Study of reaction kinetics

In a typical biodiesel production, 3 mol of alcohol react with 1 mol of triglyceride. Methanol is most often used in this reaction because of its suitable physical and chemical properties (Mahesh et al., 2015). According to Vujicic et al. (2010) and Birla et al. (2012), this transesterification can be assumed a single step reaction. The rate law of the reaction can be presented by Eq. (1):

$$-r_a = \frac{-d[\text{TG}]}{dt} = k' \cdot [\text{TG}] \cdot [\text{MeOH}]^3 \quad (1)$$

where [TG], [MeOH] and k' are concentration of triglyceride, concentration of methanol, and the equilibrium rate constant, respectively. During the reaction, excess amount of methanol was used to shift the equilibrium toward the product thus methanol concentration was considered constant. Therefore, the reaction behaves as a

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