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Rice husk-derived sodium silicate as a highly efficient and low-cost basic heterogeneous catalyst for biodiesel production

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ABSTRACT

In the present work, rice husk-derived sodium silicate was prepared and employed as a solid catalyst for simple conversion of oils to biodiesel via the transesterification reaction. The catalyst was characterized by TG–DTA, XRD, XRF, FT-IR, SEM, BET and Hammett indicator method. Under the optimal reaction conditions of catalyst loading amount of 2.5 wt.%, methanol/oil molar ratio of 12:1, the prepared catalysts gave 97% FAME yield in 30 min at 65 °C, and 94% FAME yield in 150 min at room temperature. The transesterification was proved to be pseudo-first order reaction with the activation energy (*Ea*) and the frequency factor (*A*) of 48.30 kJ/mol and 2.775×10^6 min^{-1} respectively. Purification with a cation-exchange resin efficiently removed all soluble ions providing high-quality biodiesel product that meets all the ASTM and EN standard specifications. Rice husk-derived sodium silicate showed high potential to be used as a low-cost, easy to prepare and high performance solid catalyst for biodiesel synthesis.

1. Introduction

As issues relating to energy and environment are of main concern in the past decades, research on alternative and sustainable energy has gained considerable interest. Biodiesel (fatty acid methyl ester, FAME) is a good candidate for replacing petrol–diesel fuel because it can be used in any diesel-engine without modification [1–3]. It is also clean, renewable, biodegradable, environmentally friendly and inexpensive [4,5]. Generally, biodiesel can be produced via a direct transesterification reaction of vegetable oils or animal fats and alcohols in the presence of a catalyst [6–8]. Commonly, KOH, NaOH and CH_3ONa are widely used as a homogeneous basic catalyst because they have high catalytic activity which can complete the reaction in 1 h under mild conditions at 40–60 °C [9]. Nevertheless, the use of these catalysts still involves many problems such as difficult catalyst separation, soap formation and reactor corrosion. In addition, large amount of water is usually required to wash the biodiesel product to eliminate the catalysts which leads to the increase in the overall production cost and the environmental problems [3].

On the other hand, heterogeneous catalysts can be easily separated through filtration, reused and recycled several times and require no neutralization or washing process. In addition they can also produce a high purity glycerol by-product. Hence, heterogeneous-catalyst is an efficient and more cost-effective tool to produce biodiesel [7,10,11]. There are several reports on biodiesel production using heterogeneous catalysts such as Mo–Mn/γ-Al_2O_3–MgO [12], KOH/bentonite [13], Li_4SiO_4 [14], $LiAlO_2$ [15] and CaO–La_2O_3 [16]. However, some of these catalysts still have to be developed because they show low catalytic activity, complicate to generate and absorb CO_2 and H_2O in air easily.

Calcium oxide (CaO) is one of the most studied catalysts material as it has lower price, non-toxicity, less solubility in methanol and high catalytic activity. They can be prepared from natural waste obtuse horn [3], waste coral fragment [2], hydrated lime [17], ostrich eggshells [18,19], waste oyster shells [20], chicken bones [21], waste shells of egg [18,22], golden apple snail shells and meretrix venus shells [22]. Although CaO catalysts offer many advantages, in some case, the catalyzed reactions still require long reaction times (at least 3–8 h) which increased the production cost.

Sodium silicate (Na_2SiO_3) with formula $Na_2O{\cdot}nSiO_2$ is a well-known water–glass or liquid glass which can be easily prepared from SiO_2 and NaOH [23,24]. Na_2SiO_3 was also used as a starting reactant to synthesize mesoporous silica material [25], *n*-alkane/silica composite phase [26] and β-zeolite [27]. Recently, several

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articles report the use of calcined sodium silicate as a solid basic catalyst in the transesterification of vegetable oil (soybean oil, rapeseed oil and jatropha oil) with methanol. Sodium silicate is an effective catalyst for transesterification under mild reaction condition and short reaction time (60 min at 60 °C). Furthermore, the catalyst can be reused for at least 5 times without loss of activity [28–31].

An important focus of this work is to present a simplified way to synthesize sodium silicate from rice husk which is scrap from agricultural and to use the obtained material as a low-cost basic heterogeneous catalyst in biodiesel production. The rice husk-derived sodium silicate were characterized and tested in the production of biodiesel using oils and methanol. Several parameters, such as catalyst amount, methanol/oil molar ratio, reaction temperature, type of oil and free fatty acid (FFAs) quantity and reusability were investigated. Fuel properties of the obtained biodiesel after purification and treatment process were evaluated by American Society for Testing and Material (ASTM) methods and European Standard methods (EN14214) for bio-auto fuels. In addition, reaction kinetics of transesterification using sodium silicate obtained from rice husk was investigated and compared with CaO catalysts.

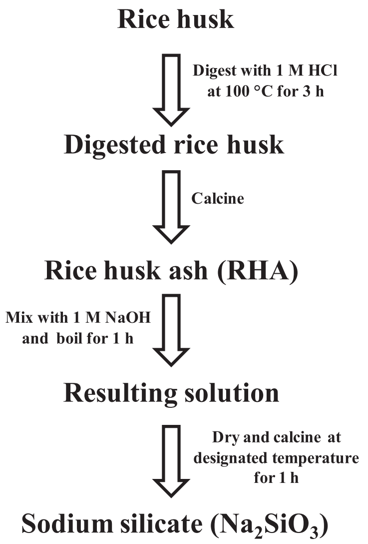

Fig. 1. Flow diagram of the sodium silicate preparation.

2. Materials and methods

2.1. Materials

Many kinds of oils containing various amounts of FFAs including palm oil (acid value of 0.32 mg KOH/g oil), lard oil (acid value of 0.42 mg KOH/g oil), coconut oil (acid value of 0.28 mg KOH/g oil), sunflower oil (acid value of 0.20 mg KOH/g oil), soybean oil (acid value of 0.27 mg KOH/g oil), rice bran oil (acid value of 0.18 mg KOH/g oil), jatropha oil (acid value of 1.31 mg KOH/g oil) and waste cooking oil (acid value of 2.31 mg KOH/g oil) were obtained from commercial sources in Thailand and were used without any purification. The analytical grade methanol, Hammett indicators (phenolphthalein, thymolphthalein, indigo carmine, 2,4-dinitroaniline and 4-nitroaniline) and sodium hydroxide (NaOH) were purchased from Fluka and Sigma–Aldrich Chemical. Calcium oxide (analytical grade CaO_AR) was purchased from Acros Chemical Co. Ltd. Rice husk collected from a local rice mill was washed with deionized water and dried at 110 °C overnight before uses.

2.2. Catalyst preparation and characterization

Fig. 1 shows a flow diagram of the sodium silicate preparation. The dried rice husk was first digested by reflux method using 1 M HCl at 100 °C for 3 h, washed with water several times and dried at 110 °C overnight. After that, white rice husk ash (RHA) was obtained by calcining the digested rice husk at 700 °C for 3 h to remove organic contains as shown in Fig. S1 in the Supporting Information [32]. The carbon residue content in the obtained RHA was determined by a CHN 628 LECO Instruments. Next, 10 g of the obtained RHA and 100 mL of 1 M NaOH were mixed and boiled in a covered 250 mL Erlenmeyer flask for 1 h with constant stirring. After that, the resulting solution was dried in an oven at 110 °C for 6 h. Finally, the resulting materials were calcined in a furnace at designated temperature (200–500 °C) in air for 1 h to generate sodium silicate materials.

Both the uncalcined and calcined materials were analyzed by X-ray powder diffraction (XRD) using a Bruker D5005 X-ray diffractometer with Cu Kα radiation (k = 1.5418 Å). Elemental compositions of the samples were analyzed by a PHILIPS Magi X wavelength dispersive X-ray Fluorescence (XRF) spectrophotometer with 1 kW Rh Kα radiation. Scanning electron microscopy (SEM) was performed on JEOL JSM 5410LV scanning electron microscope at an accelerated voltage of 20 kV. Brunauer Emmett Teller (BET) was employed on a Bel-sorp-mini II (Bel-Japan) to investigate surface area and pore volume. The samples were characterized by Fourier transform infrared (FT-IR) spectroscopy with Perkin-Elmer FT-IR spectroscopy spectrum RXI spectrometer in the range of 450–4000 cm^{-1} with resolution of 4 cm^{-1} and potassium bromide (KBr) was used as a matrix. Hammett indicator method was applied to test the basic strength by the following indicators with different acidity functions ($H\_$); phenolphthaleine ($H\_$ = 9.8), indigo carmine ($H\_$ = 12.2), 2,4-dinitroaniline ($H\_$ = 15.0) and 4-nitroaniline ($H\_$ = 18.4). The amount of basicity was measured by benzoic acid titration method using various Hammett indicators [28].

2.3. Catalytic tests and product analysis

The transesterification was carried out in a three-neck round bottom batch reactor equipped with a reflux condenser, a magnetic stirrer (300 rpm) and a thermocouple. Palm oil was used as starting material to optimize reaction condition. A mixture of solid catalyst and methanol were preheated at designated temperature (55, 60, 65 and 70 °C) and added to 30 mL of oil. The transesterification reaction was performed with various catalysts loading amount (0–5.0 wt.% relative to oil weight) and methanol to oil molar ratios (3:1–11:1).

To follow the reaction progress, 0.5 mL of solution mixture was sampled and heated in an oven at 80 °C for 3 h to remove excess methanol before biodiesel yield analysis. Proton nuclear magnetic resonance (^1H NMR) on a Brüker Ascend™ 500 MHz spectrometer was employed to evaluate biodiesel yield in term of the fatty acid methyl ester yield (%FAME). Tetramethylsilane (TMS) and $CDCl_3$ were used as the internal reference and a solvent, respectively [2,17]. The example of the obtained ^1H NMR spectrum is presented in Fig. S2 in the Supporting Information. The biodiesel yield was calculated in term of %FAME according Eq. (1):

$$\%\mathrm{FAME} = \frac{2A_{CH_3}}{3A_{CH_2}} \times 100 \tag{1}$$

where A_{CH_3} is an integration of the methoxy protons of the methyl ester moiety (CH_3—OCO—) at 3.66 ppm chemical shift. A_{CH_2} is an integration of the proton in α-carbonyl methylene groups (R—CH_2-—OCO—) both in triglyceride and methyl ester at chemical shift of