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Synthesis and catalytic activity of hydration–dehydration treated clamshell derived CaO for biodiesel production

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ABSTRACT

Biodiesel has gained interest of most researchers recently as an alternative for fossil diesel fuels in promoting environmentally sustainable fuels. With the presence of base catalyst, biodiesel can be easily produced via transesterification of triglyceride with alcohol under mild reaction conditions. Utilization of green catalysts from natural waste shells for biodiesel synthesis is capable of reducing the cost of catalyst which is beneficial to overall production cost. In this study, we have developed a modified CaO catalyst from natural waste clamshell (*Meretrix meretrix*) via hydration–dehydration treatment for transesterification process. The effects of hydration duration on clamshell were investigated to achieve the most optimum characteristic and catalytic activity. The surface area and the basicity of the treated catalyst increased extensively with prolonged hydration duration technique. By prolonging the water treatment process, it shall allow more formation of Ca(OH)₂ which then has promoted the formation of Bronsted base sites for higher basicity. The catalytic activity of hydration–dehydration treated catalysts were found increased in the following order CS-CaO_{12h} > CS-CaO_{9h} > CS-CaO_{6h} > CS-CaO_{3h} > CS-CaO_{1h}. The triglyceride conversion was as high as 98% when utilizing CS-CaO_{12h} under reflux conditions of methanol: oil molar ratio of 9:1, catalyst amount is 1 wt% and 2 h of reaction time.

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1. Introduction

Recent studies have reflected the forthcoming reduction of the fossil fuels reserves along with the rapid growth of world populations and urbanization. These scenarios have led to increasing demand for petroleum derived energy for daily necessities. Generally, increment of fuel consumption shall lead to depletion of petroleum resources in the soonest future. As this conventional energy is not renewable, therefore the world peak oil production is about to happen in another 20 years or in a decade (Rahman, 2010). In which we shall be

able to see the price tag of fossil fuel to be sky-rocketing when the demand is higher than the supply. New renewable energy source (biodiesel) was developed to meet the current industrial demands and society needs. In chemistry, biodiesel is a mixture mono alkyl ester derived from triglycerides via transesterification reaction. Transesterification involved the reaction between triglycerides (vegetable oil or animal fats) and methyl alcohol in presence of catalyst to form biodiesel and glycerol as a by-product (Roschat et al., 2012). Biodiesel is a fuel with similar fuel properties to standard fossil diesel. It is a non-toxic biofuel with higher biodegradability

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(four times faster) than petroleum diesel (Boey et al., 2010; Ngamcharussrivichai et al., 2007).

Nowadays, researchers have made attempts to seek for cost-effective and eco-friendly catalyst for transesterification reaction. Industrial waste i.e. fly ash and natural calcium source from municipal waste i.e. egg-shell, mollusk, bone, etc. are potential raw material for catalyst preparation which would eliminate wastes and simultaneously developed new low cost, highly efficient solid catalyst for sustainable green energy. Preparation of a novel low cost heterogeneous catalyst from industrial and municipal wastes is a must to synthesize fuel grade biodiesel which shall in turn valorise the wastes. Generally, natural waste shell was generated from food processing and manufacturing plants. Most of the waste shells were disposed in landfills without any pretreatment because it was traditionally useless. Waste shells are mainly composed of 95% of calcium carbonate minerals (calcite, aragonite). This is potential to be converted into calcium oxide (CaO) to act actively as solid base catalyst for transesterification process. Several types of Ca sources have been used as green CaO catalyst for biodiesel synthesis, this included eggshell (Khemthong et al., 2012; Niju et al., 2014; Oliveira et al., 2013), snails (Birla et al., 2012; Viriya-Empikul et al., 2012), mudcrabs (Boey et al., 2009), cockles (Boey et al., 2010), scallops (Buasri et al., 2013), mussels (Sharma et al., 2010), oysters (Nakatani et al., 2009), waste capiz (Suryaputra et al., 2013), white bivalves (Girish et al., 2013), bovine bone (Smith et al., 2013), cuttle bone (Viriya-Empikul et al., 2012) and sheep bone (Obadijah et al., 2012). In summary, the waste shells derived CaO rendered high transesterification activity with >98% of triglyceride conversion and biodiesel selectivity.

Although many studies have reported production of biodiesel by using waste shell derived CaO, however, the catalytic performances are still lower than commercial CaO. Generally, commercial CaO (derived from limestone) renders high transesterification activity within short reaction time. Calero reported high conversion rate of sunflower oil (100%) to biodiesel was achieved under 6:1 of methanol:oil molar ratio, 7 wt% commercial CaO catalyst, 65 °C within 1 h of reaction time (Calero et al., 2014). However, waste shell derived CaO required longer reaction time (>2 h) in order to reach high triglycerides conversion to biodiesel (Boey et al., 2009; Buasri et al., 2013; Girish et al., 2013; Obadijah et al., 2012). This is due to lower basicity and surface area of waste shell derived catalyst compared to commercially available CaO.

In present study, modification of waste shell derived CaO via thermal hydration–dehydration technique is proposed in order to improve the catalyst's characteristic such as textural properties, basicity, transesterification activity and reusability. Due to the high availability of clams (*Meretrix meretrix*) in Malaysia, the clamshell was selected as calcium source for transesterification catalyst synthesis. Similar species (*Meretrix meretrix*) of clamshell derived CaO has been investigated by Nair's research group for transesterification of frying oil (WFO). The study showed that high catalytic activity of calcined clamshell (900 °C for 3.5 h) with >89% of biodiesel obtained under reaction time of 3 h and 3 wt% of catalyst loading (Nair et al., 2012). This indicated that calcined clamshell is a potential green alternative to commercial CaO catalyst in biodiesel production. Thus, in the present study, clamshell derived CaO (*Meretrix meretrix*) is treated using hydration–dehydration treatment at various time duration (1–12 h) in order to modify and improve the chemical textural properties to induce high transesterification reactivity.

Treated catalysts are characterized using X-Ray Fluorescence spectrometer (XRF), thermogravimetric analysis (TGA), X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) surface area measurements and the basicity is determined using temperature programme desorption of carbon dioxide (TPD-CO₂). Furthermore, correlations between catalyst's properties (no treatment, hydration treatment, hydration–dehydration treatment) and catalytic activity is being investigated. The optimization study with several transesterification parameters such as methanol to oil ratio, reaction time and catalyst amount are also studied in order to obtain maximum conversion of biodiesel.

2. Experimental

2.1. Material

The clamshell (*Meretrix meretrix*) was collected from sandy Beach Remis area in Selangor, Malaysia. The shell is thick, smooth, devoid of any sculpture and triangular ovate in shape, yellowish with brown tinted coating. The refined palm olein (cooking oil) was purchased from supermarket. Methanol (99% purity) was purchased from J. Kollin Chemical and calcium oxide (CaO) of analytical grade was purchased from Sigma Aldrich, acetone ((CH₃)₂CO) and sodium hydroxide (NaOH) were purchased from Fisher Scientific, while hydrochloric acid (HCl) was obtained from J.T Baker.

2.2. Preparation of catalyst

The fleshy proteins that attached to the clamshells were moved by washing in hot water followed by scrapping and rinsed off with tap water for several times. Washed clamshells were dried in the oven at 100 °C overnight to remove adhering water. The dried waste clamshells were later crushed into small portion using hammer and then grinded until the solid shells turn into fine powder and sieved to 200 μm. Waste shell powder was then calcined at 900 °C for 4 h under atmosphere condition to generate active oxide phase. The combusted shell was denoted as CS-CaO (refer to Fig. 1: TGA analysis). CS-CaO was then underwent hydration–dehydration treatment, where the catalyst was first refluxed with water for 1, 3, 6, 9 and 12 h in the temperature of 60 °C. The slurry was dried in oven at 100 °C for 24 h for water removal, followed by grinding and sieving. The dried solid paste was then grinded prior to calcination treatment. The powder obtained was calcined at 600 °C for 3 h to generate mix phases (CaO and Ca(OH)₂). The treated catalysts were labelled as CS-CaO_{1h}, CS-CaO_{3h}, CS-CaO_{6h}, CS-CaO_{9h} and CS-CaO_{12 h} accordingly.

2.3. Catalyst characterization

The characterization of fresh powder clamshell was conducted using X-Ray Fluorescence spectrometer (XRF) (Philips PWI404) and Thermogravimetric analysis using Perkin Elmer Thermal Analyzer (Pyris Diamond TGA). The clamshell derived catalysts were analyzed in powder X-ray diffraction (XRD) analysis using Shimadzu diffractometer model XRD-6000. XRD analysis was carried out at ambient temperature and performed at 2θ ranging between 20° and 80°. Specific surface area and pore distribution of the catalysts was tested in BET nitrogen adsorption/desorption analyser using Thermo-Finnigan Sorpmatic 1990 series. The basicity

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