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Synthesis, characterization and performance of silica impregnated calcium oxide as heterogeneous catalyst in biodiesel production

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ABSTRACT

Currently, biodiesel is produced by performing a transesterification reaction with homogeneous base catalysts such as potassium hydroxide (KOH) or sodium hydroxide (NaOH) dissolved in methanol. This production process can provide high fatty acid methyl ester (FAME) yields under mild conditions. However, the homogeneous catalytic process suffers some drawbacks of an inevitable production of wastewater from washing process of catalyst residues and unreusability of the catalysts. Thus, in this study, it is proposed to synthesize and characterize a renewable low cost heterogeneous hybrid catalyst through utilization of waste material; rice husk and egg shell for transesterification reaction. The hybrid catalyst was synthesized via wet impregnation method and then characterized using fourier transform infrared spectroscopy, x-ray diffraction, surface area and pore size distribution and scanning electron microscopy. The composition of FAME was determined by gas chromatography analysis and the properties of biodiesel such as density, viscosity, acid value and calorific value were also analyzed. The result show that the calcium oxide (CaO) supported with silica is more effective for the production of biodiesel compared to CaO individually. Furthermore, the synthesized catalyst was able to be efficiently recyclable and repeatedly used up to 6 times. The fuel properties of biodiesel produced in this study were found to meet the specification of ASTM standards. Therefore, it can be concluded that the hybrid catalyst derived from waste materials can be an excellent catalyst in biodiesel production. In addition, developing new catalysts from rice husk and egg shell will not only solve the issue of disposal of these wastes but will also simplify the purification process, whereby the catalysts can be separated from the product more easily.

1. Introduction

Alternative fuels for diesel engines have gain importance because of diminishing petroleum reserves and the environmental consequences of exhaust gases from petroleum fueled engines (Xie et al., 2007). In this respect, biodiesel is an emerging alternative to diesel fuel derived from renewable and locally available resources which is cleaner, biodegradable, nontoxic and environmentally friendly. It is mainly produced via transesterification of vegetable oil, which is a renewable and sustainable source (Kansedo et al., 2009). In the transesterification reaction, a triglyceride reacts with an alcohol in the presence of a catalyst, producing a mixture of fatty acid methyl esters (FAME) and glycerol (Schuchardta et al., 1998). Currently, biodiesel is produced by performing a transesterification reaction with homogeneous base catalysts such as KOH or NaOH dissolved in methanol. However, the major disadvantage of homogeneous catalysts is that they cannot be reused or regenerated, because the catalyst is consumed in the reaction (Farooq et al., 2013). Moreover the separation of catalyst from products is difficult and requires more equipment which results in higher production costs (Freedman et al., 1984).

Based on these drawbacks, the use of heterogeneous catalysts could be an attractive solution. Heterogeneous catalysts can be separated more easily from reaction products and undesired saponification reactions can be avoided (Martino-Di et al., 2008). Biodiesel synthesis using solid catalysts could also lead to cheaper production costs because of reuse of the catalyst and the possibility for carrying out both transesterification and esterification simultaneously (Dora et al., 2005). A large variety of different heterogeneous catalysts have been investigated including supported catalysts (Umdu et al., 2009), alkali earth oxides (Ilgen and Nilgun, 2009) and hydrotalcites catalyst (Liu et al., 2008). Among them, CaO

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has been received much interest due to its long catalyst life, high activity and requires only moderate reaction conditions (Math et al., 2010).

Incorporating CaO on high surface area materials such as alumina (Umdu et al., 2009), zeolite (Wu et al., 2013) and silica (Chen et al., 2015a,b; Samart et al., 2010) was found be able to accelerate the catalytic activity of CaO and thus improved the biodiesel yield. Among these catalyst supports, mesoporous silica has attracted much attention due to its many excellent properties such as good thermal stability, high surface area and unique large pore structure characteristic, which reduce mass transfer limitations and allow high concentration of active sites per mass of material (Melero et al., 2012).

Albuquerque et al. (2008) reported the use of CaO loaded mesoporous silica as base catalysts for biodiesel production. The obtained catalyst has proven to be thermally more resistant and the interaction between CaO and silica is strong enough to prevent the lixiviation of the active phase in methanol. In another study conducted by Samart et al. (2010), silica was obtained from pluronic P123 polymer and was then impregnated with calcium acetate solution to produce CaO-silica catalyst. The fuel properties of the biodiesel obtained using the synthesized catalyst was found to meet all biodiesel standards. Studies by Umdu (2008) have demonstrated modified single step sol-gel method by using tetraethyl orthosilicate (TEOS) as precursor silica support oxides. It is reported that high dispersion of active phases was achieved for CaO based catalysts even with the high CaO loading of 80 wt%. Another studies regarding the silica from TEOS was conducted by Mohadesi et al. (2014), whereby the catalyst loading of 70% (CaO based on SiO_2), calcination temperature of 60 °C and acid to water ratio of 0.5 were optimal values, and the purity and conversion of produced biodiesel were 98.5 and 85.6%. Witoon et al. (2014) meanwhile prepared CaO supported on silica catalyst using sodium silicate and calcium nitrate tetrahydrate as a silica and CaO source, respectively. The incorporation of silica in the structure of catalyst was found to be enhanced diffusion of reactants to the active sites and thus leading to a significant enhancement in FAME percentage. Recently, Chen et al. (2015a,b) have utilized silica supported CaO catalyst derived from Na_2SiO_3 as raw material in biodiesel. In their study, the CaO–SiO_2 catalysts were prepared through the biomimetic silification approach under ambient conditions by dispersing the powder egg shells into $NaSiO_3$ aqueous solution. The obtained catalyst had a better reusability as the amount of Si compound increased. Unfortunately, absence of silica compound in the CaO–SiO_2 catalyst had a higher yield of biodiesel. It means that the incorporation of silica, which is obtained from sodium silicate in this study doesn't give better catalytic activity compared by using CaO individually.

However, there has been no work done on the utilization of silica supported-CaO catalyst from rice husk for biodiesel synthesis. Rice husk, a waste product of the processing of grain, is normally been used in power generation through combustion and its burning generates another residue, the rice husk ash. The presence of high amount of SiO_2 prompts its potential applicability as a low-cost catalyst support.

Therefore, in this study, it is aimed to synthesize and characterize a new low cost, highly efficient supported base catalyst through utilization of the two waste materials, which is rice husk ash and egg shell for transesterification of palm oil to yield fuel grade biodiesel. As can be highlighted, this study is focusing on the utilization of waste materials for synthesizing of valuable hybrid catalyst using a simple and green approach. The findings of this study offers a more economic solution for biodiesel production and in the same time could reduce waste disposal problems.

2. Materials and method

2.1. Materials

The virgin cooking palm oil was purchased from local market while waste cooking oil was obtained from a local restaurant in Arked Meranti, UTM. This oil was used for the transesterification reaction without further treatment and purification. For catalyst production, chicken eggshell was collected from local restaurants and raw rice husk was purchased from Qhadijah Natural Farm, which was located at Parit Buntar, Perak. Other chemicals used in this study were hydrochloric acid and methanol, are reagent grade obtained commercially from MD Interactive Sdn Bhd.

2.2. Catalyst preparation

The waste egg shells were cleaned to remove sand and flesh adhering to the shells by rinsing with distilled water several times. Then, the shells were dried in an oven at 60 °C for 24 h. After being dried, the shells were crushed and ground to fine powder. The dried crushed shells were then calcined in a furnace at 900 °C for 6 h in order to obtain CaO catalyst.

For silica preparation, dry raw rice husks were sieved to eliminate residual rice and clay particles and then washed with distilled water. After through washing, rice husks were filtered and dried in an oven at 60 °C overnight. The cleaned rice husks were converted into rice husk ash by heat–treating at 700 °C for 6 h, whereby the ash was brownish in color. Subsequently, the ash was boiled in 100 mL of 3 N of hydrochloric acid (HCl) from concentrated HCl for 1 h to get impurity free ash. The ash was then filtered, washed and dried in an oven. Finally, the ash was calcined at 700 °C for 6 h.

The hybrid catalyst of CaO and silica was prepared using wet impregnation method. A sample of approximately 5 g of CaO was added to 100 mL water to prepare aqueous solution. Then, this solution was added to an amount of silica and mixed vigorously under total reflux for 4 h at 80 °C. Subsequently, the mixture was filtered and dried in an oven. The dried mass was then calcined in a furnace at temperature of 800 °C for 3 h. The calcined mass obtained was referred as hybrid catalyst.

2.3. Catalyst characterization

The FTIR spectra of catalysts were obtained by using Spectrum One-Perkin Elmer with software spectrum v5.02. The x-ray diffractions (XRD) patterns of catalyst powders were recorded on a Bruker D8 Advance diffractometer using Ni-filter Cu Kα radiation, with a wavelength of 0.1541 nm at 40 kV and 40 mA. Powder samples were scanned in 2θ range varying from 10° to 90°. The surface are, total pore volume and pore size distribution of the catalyst were determined with AUTOSORB-1C, Chemisorption–Physisorption analyzer. Surface area was calculated by using BET equation from the adsorption branch of the isotherm in a relative pressure range from 0 to 1. The total pore volume of the catalyst was examined by N_2 physisorption method while the pore size distribution was determined form absorption branch by the Non-Local-Density-Functional-Theory (NLDFT) method. The surface morphology of the catalysts were investigated by using a JEOL JSM–6390LV scanning electron microscope, with the accelerating voltage of 50 kV. All specimens were coated with gold and then observed.

2.4. Transesterification process

The transesterification was carried out in a batch reactor. A 40 mL of oil was stirred in a 500 mL round-bottom flask equipped

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