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In situ transesterification of solid coconut waste in a packed bed reactor with CaO/PVA catalyst

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ABSTRACT

In this study, solid coconut waste and CaO/PVA was used as raw material and catalyst respectively to produce biodiesel through *in situ* transesterification. Both, raw material and catalyst were packed in a packed bed reactor. The reaction was fixed for 3 h and the mixing was kept constant at 350 rpm. The highest biodiesel yield of 95% was obtained at reaction temperature of 61 °C with catalyst loading (CaO/PVA) of 2.29 wt% and methanol to solid ratio of 12:1. CaO-waste derived catalyst has been successfully proven to be utilized as heterogeneous base catalyst for the production of biodiesel from solid coconut waste.

1. Introduction

Biodiesel is a biological sourced fuel; conventionally produced through the transesterification of vegetable oil or animal fat with alcohol in the presence of catalyst. Catalyst used in the transesterification reaction can be acid, base, or enzymes (Birla et al., 2012). Acid and base catalysts are more commonly used in the production of biodiesel as compared to enzyme catalysts because of their availability. Acid and base catalysts are categorized into two types; namely homogeneous and heterogeneous. Heterogeneous catalyst has become preference as it makes separation and regeneration of the catalyst become easier and less expensive (Sagiroglu et al., 2011).

Commonly, calcium compounds in the form of neat, loaded or supported Calcium oxide (CaO) are deployed as heterogeneous catalysts in the transesterification process. CaO has the advantages of high basicity, high catalytic activity, reusable, can be utilized at mild reaction conditions, and widely available as it can be synthesized from natural materials or wastes (Kostić et al., 2016; Moradi et al., 2015). Cumulatively, the catalyst is suitable for low quality feedstock (i.e. used/waste oil) since it is tolerable to small amount of moisture and free fatty acid (FFA) (Boey et al., 2011).

Feedstock contribute up to 75% of overall biodiesel production cost, thus, selection of low cost feedstock is crucial. Utilization of waste oils are found to be a good alternative to vegetable oils since they are cheaper, eliminate the competition with food industries and not affected by land availability (Atabani et al., 2012; Diya'Uddeen et al., 2012). Furthermore from the waste management viewpoint, using waste oils in biodiesel production helps to provide a cleaner way for disposing these wastes.

In Malaysia, coconut is the fourth important industrial crop after oil palm, rubber, and paddy in terms of total planted area (Sivapragasam, 2008). Approximately, 63% of coconut production is for domestic consumption and the rest is for export and industrial processing (Sivapragasam, 2008). Coconut waste is an inedible by-product after the extraction of coconut milk and normally utilized as fertilizer or to feed animals or left to decay on the fields (Ng et al., 2010; Sulaiman et al., 2010). Since the waste generation is relatively plenty, therefore, utilization of the solid coconut waste can help to save the environment.

In situ transesterification is a simplified process which combines the steps of lipid (oil) extraction and transesterification. It can be carried out in the presence of extraction solvent or in solvent-free mode (Bart et al., 2010). *In situ* transesterification process can help in reducing waste disposal whilst the analysis is much easier and also less expensive (Abo El-Enin et al., 2013). Reaction parameters play important roles in optimizing the process and they differ from that of the conventional process in many ways due to the dependence on both extraction and reaction (Abo El-Enin et al., 2013). In addition, *in situ* transesterification can also minimize the reaction time and the use of reagent and solvent since oil extraction and transesterification process are combined in one single process.

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The use of heterogeneous catalyst is promising in reducing production cost of biodiesel and waste heterogeneous catalysts have become recent interest. The shells of oysters and chicken eggs have been evaluated as effective catalysts to convert vegetable oil to methyl ester (Boey et al., 2011). Nakatani et al. (2009) showed that by using 25 wt% of thermally activated (at 700 °C) oyster shell at 6:1 methanol:oil molar ratio, the yield of biodiesel production is over 70% and purity of 98.4% was achieved in a 5 h reaction time. The conversion at a moderate 6:1 (methanol:oil) ratio was achievable at the expense of a higher catalyst and longer reaction time. Soybean oil was transesterified with 3 wt% of calcined egg shell at 1000 °C to obtain over 95% yield in 3 h reaction time with the conditions of 9:1 methanol:oil molar ratio and a 65 °C reaction temperature (Wei et al., 2009). In addition, Wei et al. (2009) found that waste catalyst is capable of being reused up to 13 times without much loss in the activity.

In this present study, solid coconut waste was used as the feedstock for biodiesel production by *in situ* transesterification using polymer-supported catalyst. Solid coconut waste is the by-product of coconut milk extraction from coconut flesh. The waste contains more than 20 wt% oil content which can be utilized to produce biodiesel (Sulaiman et al., 2013a). This study was aimed to optimize the effect of temperature, catalyst amount, and methanol to solid ratiofor maximum biodiesel yield using packed bed *in situ* transesterification process.

2. Materials and methods

Solid coconut waste (SCW) was collected from coconut milk vendor at Pasar Besar Gombak, Malaysia whilst eggshells were collected from cafeteria of International Islamic University Malaysia (IIUM). Eggshells were cleaned and SCW was sieved to eliminate any impurities. Both wastes were then placed in drying oven for 24 h at 90 °C to remove excess moisture. Then, the dried eggshells were ground finely into powder form.

2.1. Catalyst preparation

SCW and eggshells were mixed with ratio of 5:1 and then undergone calcination process at 900 °C for 4 h under static air. Calcined powdered catalysts were sieved and stored in a desiccator before use.

2 g of PVA was dissolved in 30 mL distilled water at 60 °C with continuous stirring for 4 h. After PVA was completely dissolved, the calcined catalyst was added at different concentration. The solution was continuously stirred with constant heating until homogeneous solution was achieved. Then the solution was casted on petri dish and allowed to dry in 65 °C air dryer for 24 h. The dried PVA-supported catalysts were stored in sealed plastic bag prior to use.

2.2. Catalyst characterization

The morphology and microstructures of the calcined catalyst as well as the PVA-supported catalysts were captured using scanning electron microscopy (SEM). The SEM images were obtained from JEOL Scanning Electron Microscope (JSM-5600) equipped with an energy dispersive spectroscope (EDS).

The surface area of the calcined mixture of SCW and eggshells was analyzed by BET surface analysis using Micro Active 2.00 TriStar II 3020V1.04. The analysis bath temperature was set at 77.350 K. Nitrogen was dosed into the tube above atmospheric pressure. The nitrogen was allowed to condense and the vapour pressure of the nitrogen was monitored by a transducer throughout the analysis. Te X-ray diffraction (XRD) characterization of the wastes, calcined catalyst and PVA-supported catalyst were performed on a Shimadzu X-ray diffractometer (XRD-6000). The XRD patterns were obtained with Cu K_β radiation to study the structure transformation of the catalysts on calcinations.

The presence of functional groups and the component present in the catalyst were analyzed using Fourier Transform Infrared (FTIR) Spectrometer (Thermo Fisher Scientific) equipped with Omnic software filled with FTIR region. Calcium oxide test method for biodiesel catalyst was employed using KBr technique with wave number range of 500–4000 cm^{-1} and the number of scan was 16. The transmission of KBr pellets was done by adding 5% of sample to 0.25 g KBr before pressed at 700 MPa (Lengyel et al., 2009).

2.3. In situ transesterification

In situ transesterification was conducted in a packed bed system. The packed-bed system was installed using a glass column, peristaltic pump, three-necked round bottom flask, and condenser as shown in Fig. 1. The glass column was loaded with PVA-supported catalyst, feedstock and sponge to act as the packed-bed reactor. A peristaltic pump was attached to promote the continuous flow of solvent and oil in the system. Mixing and heating were provided by a digital hotplate magnetic stirrer.

2 g of solid coconut waste was loaded into the packed bed column with different concentration of catalyst. The solvent mixture was added to a jacketed three-necked round bottom flask and being transferred into the packed bed by peristaltic pump. In this study, the reaction temperature, methanol to solid ratio and catalyst concentration were varied from 55 to 65 °C, 8:1 to 12:1, and 0.5 to 5.5 wt%, respectively as shown in Table 1. The mixture was removed after the 3 h reaction and placed in drying oven for 24 h to evaporate excess methanol. Then the samples was washed twice using warm distilled water to neutralize the pH and eliminate traces of glycerol (Birla et al., 2012). The determination of concentration of methyl ester was done using GCMS.

The optimization of methyl ester was conducted using Design Expert 6.0.7 (Stat-Ease Inc., USA). The optimal reaction condition and the relationship between the three reaction parameters were investigated using Response Surface Methodology (RSM) and Central Composite Design (CCD). The upper temperature level was set to 65 °C since it is the boiling point of methanol, any temperature above that will cause it to evaporate in which there will be mass transfer limitation and bubble formation of methanol.

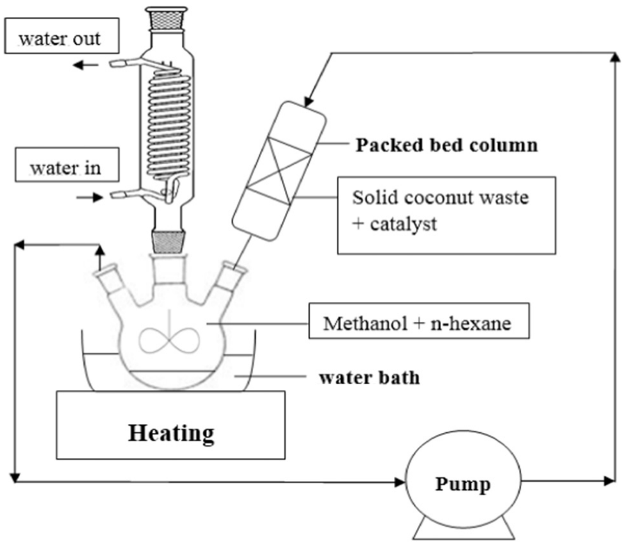

Fig. 1. Experimental set-up for packed bed *in situ* transesterification.