

Optimization of biodiesel production by solid acid catalyst derived from coconut shell via response surface methodology



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ABSTRACT

The application of solid acid catalyst in biodiesel production eliminates the tedious pretreatment of feedstock and eradicates generation of high volume of wastewater. A novel acid catalyst was prepared via sulfonation of incompletely carbonized coconut shell using concentrated sulfuric acid. The design of experiments were performed using four factor-three-level central composite design coupled with response surface methodology to evaluate the interaction between two factors in order to determine the optimum process conditions. A quadratic model was suggested for the prediction of biodiesel yield. The F-value and p-value of the model were 4.02 and 0.0129, respectively, indicate that the model was statistically significant at 95 per cent confidence interval. In addition, R^2 value of the model was 0.8364, which indicates the acceptable accuracy of the model. From the optimization study, it was found that the carbonization temperature, carbonization time, sulfonation temperature and sulfonation time were 422 °C, 4 h, 100 °C and 15 h, respectively. At these optimum conditions the predicted and observed biodiesel yield were 88.15 per cent and 88.03 per cent, respectively, which experimentally verified the accuracy of the model. The use of coconut shell-derived solid acid catalyst in biodiesel production promotes the sustainable and green way of operations.

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1. Introduction

Biodiesel is an environmental friendly solution for fuel and power generation. Due to greater concern on environmental pollution caused by over consumption of petroleum product and scarcity of the resources has turned the world's interest into biodiesel production (Leung et al., 2010). Biodiesel is mainly derived from vegetable oils of animal fats through chemical reaction of methanol that result in the formation of fatty acid methyl ester and glycerol as by-product (Borges and Diaz, 2012). The general representation of transesterification reaction is illustrated in Fig. 1. Generally, 3 mol of methanol is required to convert and break down

the long branched triglyceride compound into diglyceride and monoglyceride respectively. As a result, fatty acid methyl ester (FAME) can be obtained as the main transesterification product (Abdullah et al., 2017). Numerous studies conducted on biodiesel found that it is non-toxic, less harmful, produce cleaner emission and did not contribute to global warming (Ahmad et al., 2011; Sumprasit et al., 2017). Hence, biodiesel is considered to be a biodegradable and renewable source of fuels that is far more practical than fossil fuel (Ashnani et al., 2014).

In a large scale application, biodiesel is commonly produced using transesterification reaction catalyzed by base catalyst such as NaOH or KOH due to fast reaction time (Konwar et al., 2014).

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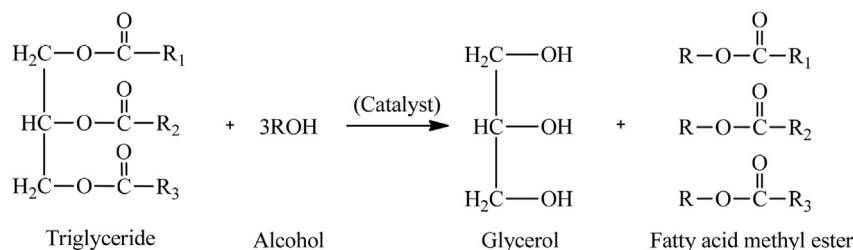


Fig. 1. General transesterification reaction scheme (Abdullah et al., 2017).

However, the process requires pre-treatment of feedstock to reduce their free fatty acid (FFA) content to prevent from soap formation in the latter (Tariq et al., 2012). On top of that, generation of high volume of wastewater as a result of washing and purification steps present environmental threat to the receiving water (Helwani et al., 2009). On the other hand, heterogeneous catalyst eliminate the generation of wastewater and can be easily separated (Lam et al., 2010).

Application of biomass derived as solid acid catalyst in biodiesel production has been widely explored (Dehkhoda and Ellis, 2013; Ayodele and Dawodu, 2014; Prabhavathi Devi et al., 2014). Solid acid catalyst derived from biomass exhibit high catalytic activity thus resulted in high biodiesel conversion. For example, Ezebor et al. (2014) studied the potential of sugarcane baggase and oil palm trunk as catalyst with 94 per cent and 93 per cent conversion of biodiesel could be achieved in the transesterification of palm olein. In another study, Li et al. (2014) reported that rice husk char showed high catalytic activity (88 per cent) in the transesterification of waste cooking oil. Since the solid acid catalyst is mainly derived from waste material, it is basically low cost and abundance in supply (Emrani and Shahbazi, 2012). Apart from that, it creates a potential market value for unwanted biomass (Sanjay, 2013).

Response surface methodology (RSM) is a numerical tool that is widely used for optimization study in large number of chemical processes (Tabaraki et al., 2014; Jabeen et al., 2015). It is a set of mathematical technique that describes the relationship of several individual variables with one or more response (Witek-Krowiak et al., 2014). It exterminates the one-factor-at-a-time method that produces large number of experimental run and rather time consuming. Furthermore, RSM is able to evaluate the interaction effect of two or more variables to the response that allows better understanding of the process. Apart from that, RSM allows the determination of the best level of factors to optimize the desired output (Choi et al., 2016).

Coconut shell (*Cocos nucifera*) belongs to the family of *Arecaceae* is considered as one of the major agricultural waste in Malaysia. In 2009, it was estimated around 0.459 million tonnes coconut was produced in Malaysia. This has led to production of significant amount of biomass. The major contributors are coconut shell (0.735 million tonnes), coconut husk (0.166 million tonnes), coconut frond (0.103 million tonnes) and empty bunches (0.022 million tonnes) throughout the year (Sulaiman et al., 2017). Biomass displays great potential to be a starting material for industrial process as it is less expensive and does effect food supplies (Farah et al., 2016). Re-use of waste material is greatly desired towards developing environmentally safe biodiesel processing. Coconut shell is abundantly available and comes from renewable resources (Prauchner and Roriguez-reinoso, 2012; Sani et al., 2015). On top of that, coconut shell is rich in carbon, low ash content, high in strength and hardness make it suitable for catalyst development (Hidayu and Muda, 2016).

In this study, a novel carbon based solid acid catalyst was

prepared by the sulfonation of incompletely carbonized coconut shell. The effect of preparation variables including carbonization temperature, sulfonation temperature and holding time on the structure and activity of catalyst were systematically investigated. The catalysts were employed in the transesterification of palm oil with methanol. On top of that, the optimal conditions for catalyst preparation was also evaluated.

2. Materials and methods

2.1. Materials

Coconut shell was locally obtained from daily market. Proximate analysis was performed in accordance to the ASTM standard to determine its characteristic including moisture (D2867), ash (D3174), volatile matter (D3175) and fixed carbon. Palm oil (BURUH) was purchased from local grocery store. Concentrated sulfuric acid (98 per cent), methanol and sodium hydroxide (NaOH) were purchased from Merck. Hydrochloric acid (HCl), sodium chloride (NaCl) and potassium hydroxide (KOH) were purchased from Sigma-Aldrich.

2.2. Catalyst preparation

The biomass was primarily washed with distilled water to remove impurities then sliced into thin pieces (<2 cm) and sundried for 24 h. The sliced biomass was then subjected to oven-drying at 100 °C for 12 h to remove any moisture. About 20 g of the precursor carbon catalyst was incompletely carbonized through in a muffle furnace for a certain period of time. The carbonized sample was then ground in a laboratory mortar to form fine powder (0.5–1 mm). Sulfonation of activated carbon was conducted by mixing of 10 g carbon catalyst with 100 ml H₂SO₄ in a 250 ml conical flask for 15 min. Excess acid was removed. The residual wet solids (carbon and acid) were then transferred to a ceramic crucible placed in a muffle furnace and heated at desired temperature for specified time. After cooling to ambient temperature, the sulfonated carbon catalyst was washed with excessive distilled water until the wash water became neutral and dried at 105 °C for 10 h in an air-drying oven. Sulfonated carbon catalyst was kept in an air-tight container to prevent contamination.

2.3. Catalyst characterization

The surface area and pore volume were determined using Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) equation with the aid of nitrogen gas adsorption/desorption technique using Micromeritics V4.02. Samples were degassed prior to analysis. Surface morphology of the catalyst with Scanning Electron Microscopy (SEM) was performed using SEM-JEOL unit with 10 kV accelerating voltage. The total acid density of the prepared catalyst was measured using acid-base back titration method described by Ezebor et al. (2014). Titration was performed three times and the

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