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Transesterification of used cooking oil over alkali metal (Li, Na, K) supported rice husk silica as potential solid base catalyst

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ABSTRACT

Investigation was conducted on three alkali metals (Li, Na, and K) supported by rice husk silica as catalysts for methyl esters production. A simple pseudo-heterogeneous transesterification process of used cooking oil with methanol was conducted to produce methyl esters using calcined alkali metal supported rice husk silica as a solid catalyst. Alkali metal silicate catalysts showed longer lasting activity than the traditional alkali catalysts. The optimum conditions for the process were: alkali metals silicate calcination temperature 500 °C, time 3 h; catalyst amount 3%; methanol to oil molar ratio 9:1; and a reaction temperature of 65 °C. The process was able to transesterify oil to methyl esters in the range of 96.5–98.2% in 1 h for all series. The catalyst is able to tolerant free fatty acid and moisture up to 1.25% and 1.75%, respectively. The catalyst was easily separated from the reaction mixture by filtration and able to reuse six times. The final product met the selected biodiesel fuel properties in accordance with European Standard (EN) 14214.

1. Introduction

The global oil consumption in 2010 grew by 2.7 million barrels per day (b/d), or 3.1%, to reach a record level of 88 million b/d, while the fossil fuel reserve is depleting [3]. Furthermore, petroleum-based activities are one of the main causes of carbon dioxide (CO_2) emission to the atmosphere. The transportation and industrial sector are almost entirely dependent on petroleum-derived fuels, which accounted for respectively 12.2 and 4.6 million b/d of oil consumption in January 2012 [8]. This scenario has driven the EU, the USA, Brazil, and parts of Asia to import renewable energy.

Biodiesel is one of the energy sources that can be used as an alternative fuel for diesel engines. Such data demonstrates the global awareness of the limitations of the fossil fuel and the quest for new energy alternatives. The common feedstocks for biodiesel are vegetable oils and animal fats. Thus, it can be said that the major lipid for biodiesel production comes from edible oils. However, as feedstock accounts for approximately 80% of the operational cost [9], the feedstock price has a huge effect on the overall production cost. In addition, consuming edible oil for biodiesel competes with food supply and has a definite impact on global food security and land.

One way to reduce the production cost is by utilizing used cooking oil (UCO). The source is abundant supply, relatively inexpensive and the utilization offers benefits on environmental conservation [25]. In addition, it is low in price in terms of its operational cost and feedstock, and recycling technology can be applied during the process. However, the UCO contains free fatty acid (FFA) and moisture. FFA content in waste oil should be as low as possible for alkali-catalysed transesterification and alkali catalysts will readily react with FFA to form soap if FFA content above 2.5% present in the reaction media [2]. This reaction is highly unfavourable because it will deactivate the catalyst from accelerating the transesterification reaction. Furthermore, too much soap in the product can drastically reduce the methyl esters (ME) yield and inhibit the subsequent purification process of biodiesel, including glycerol separation and water washing. Recently, the production of biodiesel by transesterification method using solid catalysts has become more favourable compared to others and has been scaled up to industrial level. Solid base catalysts bring several advantages, such as the catalyst can easily be separated from the reaction mixture, no washing is required, easy regeneration, less

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corrosive character of the product, low in cost and it is a more environment friendly approach.

There is a very limited work on comparing alkali metals supported by silica from rice husk ash (RHA) as a catalyst in transesterification. RHA was utilized as a catalyst support for Li in transesterification of soybean oil [6]. RHA as biomass has promising role with high silica content (87–99%) and available abundantly, being a low cost waste source as amorphous silica precursors [24]. Each tonne of rice produces 200 kg of rice husk, and with the complete combustion will be generated 40 kg of RHA [21]. Recently, about 146 million tonnes of RHA was produced annually worldwide [10] and efforts are being made to overcome this environmental issue by utilization this material as support. Accordingly, in this study RHA is used as a supporting material for alkali metals (Li, Na, K), which are considered as strong base catalysts. The base catalysts are prepared using a simple impregnation method. The effect of a catalyst structure on alkali metal silicate and reaction parameters (catalyst amount, methanol to oil molar ratio, reaction duration and reaction temperature) on the ME content will be investigated. Furthermore, their tolerance towards water and FFA will also be discussed.

2. Material and methods

2.1. Materials

The raw material used in this work is UCO, (acid value was found to be 3.54 ± 0.05 mg KOH/g, equivalent to 1.77% FFA (as oleic acid) and 0.28% ± 0.04 of moisture content), which was collected from a local restaurant. RHA was collected from rice mills in Kedah, Malaysia. The chemicals purchased from Sigma–Aldrich (Switzerland) including sodium hydroxide, lithium hydroxide, potassium hydroxide all were of analytical grades, phenolphthalein ($H\_ = 8.2$), 2,4-dinitroaniline ($H\_ = 15.0$) and 4-nitroaniline ($H\_ = 18.4$) and methyl heptadecanoate as an internal standard GC grades (>99.1%). Methanol (anhydrous, ≥99.8%), sulphuric acid (95–97%), and hexane (anhydrous, ≥99.8%) were supplied by Hamburg (Germany), hydrochloric acid (37% HCl) and $CDCl_3$ for NMR was purchased from Merck and Cambridge Isotope Laboratories, Andover, MA (USA), respectively.

2.2. Preparation of rice husk silica

RHA was macerated with a porcelain mortar and sieved with a 200 mesh sieve. Then, 10 g of powdered ash was washed with 60 mL of 0.1 mol L^{-1} HCl for 1 h, and neutralized with deionized water. The washing step is to remove the trace of minerals/metal (Al, Ca, K, Mg, Mn and Na) contained in RHA [14,19] and organic compounds. Finally, the clean ash was dried in an oven at 105 °C for 2 h. The purified RHA is labelled as rice husk silica (RHS).

2.3. Preparation of alkali metal silicate and acid silica catalysts

Alkali metal silicates were prepared using the wet impregnation method. Amorphous RHS was suspended in water as a first step. An aqueous solution of alkali metal (sodium hydroxide, lithium hydroxide, or potassium hydroxide) was then slowly added to the suspension. All reactions were performed at $M^+OH:SiO_2$ molar ratio of 2:1 (stoichiometrical ratio) [11]. The obtained mixture was then stirred and heated at 90 °C for 2 h. Lastly, the mixture was dehydrated at 200 °C for 30 min, and then calcined at 200, 500 and 700 °C for 3 h.

Acid silica catalyst was prepared by impregnation method as follows: Two grams of RHS was added into 25 mL of 0.2 M H_2SO_4 solution. The mixture was stirred vigorously at room temperature for 2 h before drying at 100 °C for 2 days. The obtained dry powder was ground followed by calcination at 500 °C for 7 h. The samples were labelled as SO_4-silica [17].

2.4. Material characterization

The alkali metal silicate was identified by X-ray diffraction (Rigaku) with Cu Kα X-ray as a source. A FTIR (PerkinElmer Spectrum 100) spectrophotometer was used to characterize the chemical structure of alkali metal silicate at 400–4000 cm^{-1} range. Surface analysis of the catalyst was examined by using Micromeritics ASAP 2000. Prior to the analysis, all the samples were degassed at 105 °C and the adsorption of N_2 was measured at −196 °C. The size and morphology of catalyst was observed by FE-SEM (JSM-7800F). X-ray fluorescence (XRF) analysis was performed on Bruker S8 Tiger using the pressed-pellet (pressure at 8.0 Pa) method. The base strengths of the catalyst ($H\_$) were determined by using Hammett indicators. The following Hammett indicators were used: phenolphthalein ($H\_ = 8.2$), 2,4-dinitroaniline ($H\_ = 15.0$) and 4-nitroaniline ($H\_ = 18.4$). About 25 mg of catalyst was shaken with 5.0 mL of a solution of Hammett indicator diluted with methanol, and left to equilibrate for 2 h. After the equilibration, the colour change of the solution was noted. The UCO was filtered to remove visible solid materials. The acid value of the oil was determined following the standard EN 14104; and the moisture content was analysed using Karl Fischer titration method (784 KFP Titrino, Metrohm).

2.5. Transesterification

The content of UCO to ME was performed in a 50 ml 2-neck round bottom flask equipped with a reflux condenser and magnetic stirrer. The transesterification reaction between oil and methanol was carried out in the liquid phase under atmospheric pressure, at 65 °C for 1 h with continuous stirring. The effect of the molar ratio of methanol to oil (6:1–20:1 wt.%), catalyst amount (1–4 wt.%), reaction duration (0.5–5.0 h), reaction temperature (35–75 °C) and the addition of water and FFA (0.25–7 wt.%) on the reaction were investigated. After the transesterification, the reaction mixture was allowed to cool to room temperature. ME was isolated by centrifugation to further separate the layers (ME, glycerol and catalyst), and then the excessive amount of methanol and water was evaporated before the chromatographic analysis. The reaction were carried out three times in order to reflect the precision and errors of the results. The concentration of ME in the sample was determined by following the European regulation procedure EN 14103 [4]. In this study, GC–MS (Agilent Technologies, 7890A GC-System) with capillary column DB-wax (length 30 × diameter 0.25 mm × film thickness 0.25 μm) using methyl heptadecanoate as an internal standard. Helium was used as the carrier gas with a linear velocity of 40 cm/s. The oven temperature was programmed at 190 °C, held for 2 min, then ramped at 10 °C per min until it reached 230 °C, and with a final hold time of 8 min. The sample volume of 0.6 μL was injected into GC. The peaks of ME were identified by comparing them with their respective ME standards and the ME content was quantified using the following formula:

$$\text{ME content}(\%) = \frac{(\sum A) - A_{\text{ISTD}}}{A_{\text{ISTD}}} \times \frac{C_{\text{ISTD}} \times V_{\text{ISTD}}}{m} \times 100$$

where

$\sum A$ = total peak area of ME from $C_{12:0}$ to $C_{18:1}$

A_{ISTD} = peak area of methyl heptadecanoate

C_{ISTD} = concentration, in mg/mL, of the methyl heptadecanoate solution.