



PREPARATION OF BIODIESEL FROM PALM OIL DECANter CAKE WITH SULFONATING RICE HUSK ASH AS A CATALYST

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ABSTRACT

Recently, the use of waste oil especially in biodiesel industry has gain much attention because of its low price, thus lowering the economics of the commercial production cost. As such, this study present the utilizing of waste palm oil adsorbed on decanter cake as a feedstock for biodiesel production. Palm oil decanter cake, a waste originated from palm oil mill, suffered with high free fatty acids (FFA) is difficult to be converted into methyl esters via conventional basic catalyst. Therefore, a solid acid, RHA-SO₃H catalyst was prepared by sulfonating rice husk ash (RHA) with concentrated sulfuric acid, which can work for both esterification of free fatty acids and transesterification of triglycerides present in oil of decanter cake. The solid acid catalyst was characterized in detail with TGA, FTIR, BET, XRD, FE-SEM, and Hammett indicators. The RHA-SO₃H catalyst shows good catalytic activity for simultaneous esterification and transesterification of oil adsorbed on decanter cake. Under optimized reaction conditions, about 80 wt.% of methyl ester was produced at 6 wt.% catalyst, 17:1 of methanol to oil molar ratio after 5 h of reaction.

Keywords: biodiesel, esterification, transesterification, decanter cake, solid acid catalyst.

1. INTRODUCTION

Today, serious concerns over the rising levels of greenhouse gas emission, global warming and dwindling reserves of fossil fuels make the biofuels especially biodiesel being politically desirable worldwide. The biodiesel industry has steadily expanded over the past decade, has reached a state where implementation of the national alternative energy policy turns feasible. Indeed, nowadays, biodiesel use has become mandatory in several European Union (EU) countries and some countries already go advance by implementing biodiesel blend mandate. Malaysia alone has very recently successful implementing B5 (addition 5% of biodiesel and 95% of regular petroleum-based diesel) nationwide in 2014. Yet, biodiesel production is forecast to continue growing through 2015 as government of Malaysia has planned to rollout B7 (addition 7% of biodiesel and 93% of regular petroleum-based diesel) upon successful implementation of B5 mandate [1]. The idea of applying biodiesel blend mandate does increase the biodiesel usage domestically. However, higher palm oil prices (palm oil price vis-à-vis petroleum price problem) would hinder the forecast, thus continue to arrest the expansion of biodiesel industry which depend on crude palm oil (CPO) as a feedstock [2]. In view of these problems, many companies start to explore the use of waste materials from palm oil sector like palm fronds, empty fruit bunches (EFB), spent bleaching clay (SBC), palm fatty acid distillate (PFAD), decanter cake (DC) and other palm biomass as feedstock for energy production, thereby can cut off greenhouse gas emission resulting from palm oil processing.

The target of this work is to use waste from palm oil mill which is called decanter cake as a source of triglycerides to produce methyl esters (biodiesel). DC is a brown-blackish solid waste produced by oil palm mill after the solid fraction is removed from the waste water produced after the extraction of crude oil. The DC is

produced when the crude palm oil is centrifuge for purification where the sediment is called decanter cake and the supernatant is the wanted purer palm oil [3].

In line with the costing related matter, this research tends to use agricultural wastes, rice husk ash (RHA) as a support for catalytic materials. RHA was obtained during milling process after burning the rice husk (outer cover of rice grain) in air, which has pointed as agricultural waste. RHA compose large amount of silica (87-99%) together with cellulose, hemicellulose, lignin and small amount of inorganic salt [4-7]. Replacement of conventional liquid acid catalyst, which is toxic and corrosive with more eco-friendly heterogeneous solid acid catalyst, becomes the area of current interest for many researchers. There are various supports or precursors that can apply for preparation of this solid acid catalyst like silica, montmorillonite, organic polymer and zeolite. Among them, silica is one of the upmost used cases due to its ease of handling, abundantly available, low cost and non-corrosive [8]. Since RHA possesses high pozzolanic activity as having high surface area and large amount of silica content, it can be economically viable support for preparation of solid catalyst [9,10]. To the best of our knowledge, there is limited research use silica from RHA as a precursor in preparation of biodiesel. As such, this study aims to explore alternative approach to use RHA to prepare solid acid catalyst by sulfonating with concentrated sulfuric acid which can work for both esterification of free fatty acids and transesterification of triglycerides present in oil of decanter cake.

2. EXPERIMENTAL

2.1. Materials

Palm oil decanter cake (DC) with acid value of 13.8mg/KOH g was collected from local palm oil mill, LKPP Lepar, Pahang, Malaysia and rice husk ash (RHA)



was collected from rice mill in Kedah, Malaysia. Methanol, heptane, hydrochloric acid (HCl), sulphuric acid (98%), hexane, crystal violet ($H_{\text{c}}=1.8$), bromophenol blue ($H_{\text{b}}=4.6$) and methyl red ($H_{\text{m}}=6.2$) of analytical grades were purchased from Bendosen Laboratory Chemicals (Norway). The internal standard (methyl heptadecanoate) of chromatographic grade was purchased from Sigma-Aldrich (Switzerland).

2.2. Catalyst preparation

The collected rice husk was cleaned and heated at 900 °C in a furnace for 4 hours. The ash produced was macerated with porcelain mortar into fine powder. About 10g of RHA powder was weighed before washing with 60mL of 0.1M HCl for an hour. Then, the powder was neutralized (pH7) with deionized water and dried in oven overnight at 110°C. The purified powder, labelled as RHA was sulfonated with concentrated sulphuric acid (60mL) for 3 hours in an oil bath at 90 °C. The mixture was added to distilled water, stirred and filtrate after cooling at room temperature. The hot distilled water was used repeatedly to wash off the sulfate ions of the precipitate [11]. Later, the precipitate (RHA-SO₃H catalyst) was dried overnight in oven at 80 °C.

2.3. Catalyst characterization

The Hammett indicators: crystal violet ($H_{\text{c}}=1.8$), bromophenol blue ($H_{\text{b}}=4.6$) and methyl red ($H_{\text{m}}=6.2$) were used to measure the acid strength of the catalyst. The thermal stability of RHA-SO₃H catalyst was determined by Mettler Toledo TGA/DTA and the framework vibration was analysed by FTIR, Perkin Elmer Spectrum 100. The specific surface analysis was examined using Micromeritics ASAP 2000 and calculated following the Brunauer-Emmett-Teller (BET) equation. The catalyst was identified by X-ray diffraction (Rigaku) with Cu K α as a source with 2 θ range 10° -80° with step sizes of 0.1° and its scanning speed was 1° min⁻¹. The morphology study of the prepared catalyst and its elemental compositions was captured by field emission scanning electron microscopy coupled with electron dispersive X-ray (FESEM-EDX) (JSM-7800F).

2.4. Esterification and transesterification activity

The esterification and transesterification reaction was performed in a round bottom flask together with condenser, immersed in oil bath with the constituent of 2g DC-oil, solid acid catalyst (2-12 wt.%) and methanol to oil molar ratio of (9:1-21:1) at temperature of 100°C with duration time (3-9 h). The GC-FID coupled with polar capillary column (DB-Wax, 30m x 0.25mm i.d. x 0.25 μ m) was used to chromatographic analysis of the methyl esters produced following the European procedure EN 14214 using methyl heptadecanoate as an internal standard.

3. RESULTS AND DISCUSSION

3.1. Catalyst characterization

The acidic strength of the RHA-SO₃H catalyst, tested by Hammett indicators (bromophenol blue and methyl red) shows that the colors of indicators lie in the acidic form. However, the color of the crystal violet indicator lies in the basic form. Therefore, the acidic strength of the catalyst is in the range between pH 0.0 to pH 1.8 (Table-1). The TGA/DTA curve of the catalyst showed about 6% weight loss occurred from room temperature to 130 °C that indicates the evaporation of water. The second weight loss about 20% around 130 to 300 °C showed that the -SO₃H groups had decomposed to SO₂. This shows that the methanol refluxing temperature for the esterification and transesterification reaction is acceptable, as the catalyst remains stable without losing the -SO₃H groups below 130 °C. Figure 1(b) showed the FTIR spectrum of RHA and RHA-SO₃H catalyst. In RHA spectrum, broad peak around 3546.71 cm⁻¹ corresponded to the -OH stretching of SiOH and symmetry stretching of H₂O whereas the peak at 1639.56 cm⁻¹ is due to the bending of H₂O adsorbed. In RHA-SO₃H spectrum, the more broader peak appeared around 3427.63 cm⁻¹ compared to the -OH stretching of SiOH peak in RHA due to -OH stretching absorption of -SO₃H groups. The S-O stretching in -SO₃H group mode did appear in the catalyst spectra at 885.64 cm⁻¹ and 578.26 cm⁻¹, thus confirming the existence of the sulfonic group in the prepared catalyst [8, 12]. The existence of sulfonic group also been proven by the elemental analysis, EDX as depicted in Figure 1(d) which showed the existence of sulfur group (S) in the catalyst. The BET analysis revealed that the sulfonating process decreases the surface area and pore volume of RHA but increase the pore size of the RHA. The average pore size of the RHA-SO₃H catalyst is 10.7nm (mesoporous) which suit best as a catalyst for preparation of biodiesel. From the XRD patterns, they clearly indicate that the amorphous forms of the silica RHA remain unchanged even after introducing the sulfonic group. The prepared catalyst possessed spherical agglomerate structure as captured by FESEM. The modification of RHA with sulfuric acid made the catalyst became more aggregated as shown in Figure 1(c) and 1(d).

Table-1. Acid strength determination of RHA-SO₃H catalyst.

Indicators	pH range	Acidic form (<pH)	Colour change
Methyl red	4.4 – 6.2	Red (<4.4)	Remain Red
	Red – Yellow		
Bromophenol blue	3.0 – 4.6	Yellow (<3.0)	Remain Yellow
	Yellow – Purple		
Crystal violet	0.0 – 1.8	Yellow (0.0)	Yellow to Purple
	Yellow – Purple	Purple (<1.8)	

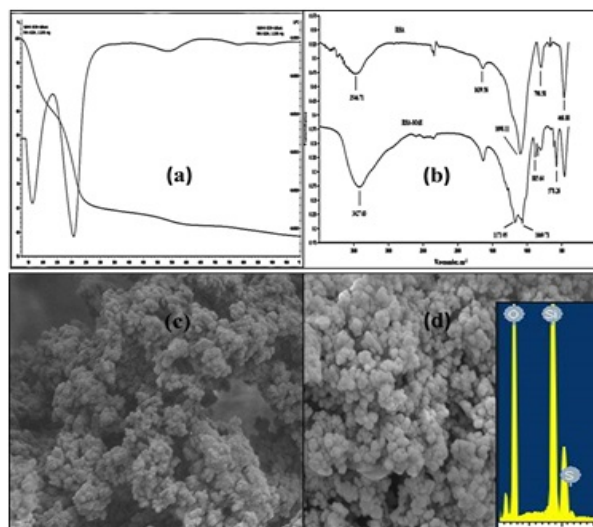


Figure-1. (a) TGA/DTA curve RHA-SO₃H catalyst, (b) FTIR spectrum of RHA and RHA-SO₃H catalyst, (c) particle morphology of RHA, (d) particle morphology and elemental analysis of RHA-SO₃H catalyst.

3.2. Effect of catalyst amount

Catalyst amount obviously showed significant effect towards the methyl esters content. As depicted in Figure-2(a), methyl esters (ME) content slightly increased with an increment of the catalyst amount, proving that both esterification and transesterification process are dependable on the catalyst amount. In this study, the ME content showed the increasing order as the catalyst amount increased from 2 to 6 wt.%. However, the ME content suddenly dropped after increasing the catalyst amount above 6 wt.%. The dropping scenario could be best explained as the result of poor dispersion of the solid catalyst into the immiscible phases of methanol and oil when the catalyst amount is in excess (excess catalyst disrupts the mixing of reactants). Other than that, the ME decline could also happen when the products (methyl ester) produced were not desorbed from the surface of catalyst if too much catalyst exist [13]. The ME could trap into excess unoccupied active site of the catalyst. Therefore, 6 wt.% catalyst loading is most acceptable amount for the present study.

3.3. Effect of methanol to oil molar ratio

As both esterification and transesterification process are reversible and endothermic, excess methanol is needed to improve reaction rate and favour forward reaction. It was in line with the obtained result displayed in Figure-2(b). The ME content increased as the methanol to oil molar ratio increased until reaching its equilibrium state before slightly decrease. Exceed the equilibrium point; methanol molecule could possibly flood the active sites rather than the DC-oil molecules which leads to low conversion [14]. Otherwise, the rate of reaction could also become slower if too much excess methanol exists as it could dilute the oil and end up with decreasing

the ME produces [3,15]. Thus, the methanol to oil molar ratio fixed the best at 17:1 with ME content of 80.5 wt.%.

3.4. Effect of reaction time

In order to reach equilibrium state, sufficient time is needed to achieve adequate contact time between catalyst and reactants. Higher ME content was achieved with increasing reaction time as illustrated in Figure-2(c) but ME decreased when further increase reaction time. Theoretically, production of water occurs during esterification process. Hence, as the reaction time increase (after equilibrium state), water produces in the reaction mixture progressively increase too resulting the ME back to FFA due hydrolysis [16]. Moreover, -SO₃H groups is hydrophilic and do favors the produced water. Excess water produce during long reaction time will deactivate the catalyst and causing the reduction of ME content. According to the result obtained, 5h was the sufficient time to achieve complete simultaneous esterification and transesterification process of DC-oil with RHA-SO₃H catalyst to yield biodiesel.

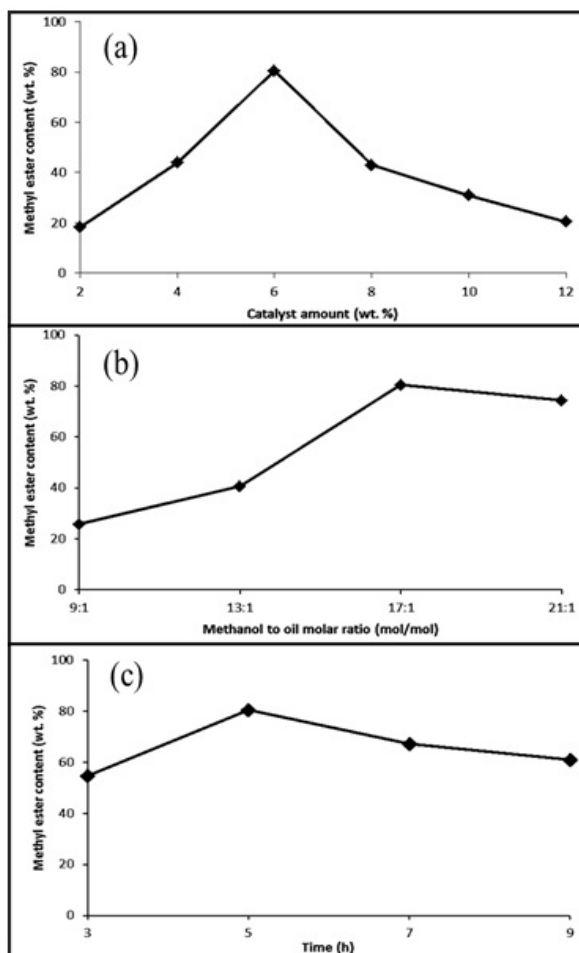


Figure-2. Effect of (a) catalyst amount; (b) methanol to oil molar ratio; (c) reaction time towards the methyl ester content.



4. CONCLUSIONS

The investigated solid acid catalyst, RHA-SO₃H can perform efficiently and simultaneously for both esterification of FFA and transesterification of triglycerides in DC-oil. As evident, the highest ME content was obtained as much as 80.5% at 6 wt.% catalyst amount, 17:1 methanol/oil molar ratio for 5h reaction time at 100 °C. As a conclusion, material derived from waste sources (palm oil decanter cake and rice husk ash) was successfully utilized as a low-cost feedstock and catalyst to produce valuable biodiesel.

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