Sustainable Development Proceedings, Volume 1, 2023 doi: 10.5281/zenodo.8398366

Sulfonic acid functionalized rice husk ash as a catalyst for esterification of palm fatty acid distillate

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Abstract

Palm fatty acid distillate (PFAD) is a valuable and low-cost raw material that promises a sustainable source of feedstock for the esterification process to produce fatty acid methyl ester (FAME) as biodiesel. Low-cost heterogeneous acid catalysts are attractive for application in making ester products. Rice husk ash, which contains a high amount of silica, is a large amount of waste from combustion to generate electricity from biomass power plants. Therefore, this research was interested in studying the preparation of rice husk ash functionalized with the sulfonic acid group to use as an acid catalyst in esterification PFAD to produce methyl ester for biodiesel. The heterogeneous acid catalyst from rice husk ash (RHA) which was prepared by immersing in H_2SO_4 solution and calcined at 700 °C, following functionalized with 3-mercaptopropyl trimetoxysilane (MPTMS) and oxidized with H_2O_2. The rice husk ash functionalized with a sulfonic acid group (RHA-SO_3H) exhibited the amorphous silica structure, specific surface area of 193 m^2/g, average pore volume of 0.98 cm^3/g, average pore diameter of 21.2 nm and acid amount 0.52 mmol/g. The esterification of PFAD with methanol was studied using a PFAD: methanol molar ratio of 1:9, catalyst loading of 1 wt% at 100 ºC for 1 h. The RHA-SO_3H exhibited the conversion of palm fatty acid distillate at 54.3%.

Keywords: Palm fatty acid distillate, rice husk ash, biodiesel, sulfonic acid group, esterification

Peer-review under responsibility of the organizing committee 1st International Conference on ASEAN Sustainable Development (ICASD 2023).

1. Introduction

Biodiesel is an alternative to conventional diesel fuel and can be produced from vegetable oils or animal fats. It is renewable and biodegradable, produces fewer air pollutants than petroleum-based diesel, and decreases our dependence on fossil fuels. Biodiesel production can be prepared via esterification, in which the carboxylic molecules in vegetable oils or animal fats chemically react with short-chain alcohols (e.g., methanol or ethanol) in an acid catalyst [1]. Esterification is an acid-catalyzed reaction. The use of solid acid catalysts for this reaction has recently been attractive due to high selectivity, ease of separation, ease of recovery, and reduced waste. It has been many reports on preparing solid acid catalysts by functionalized sulfonic group onto the framework of mesoporous silica materials. They exhibited an increase in catalytic activity and selectivity in the esterification. The rice husk ash is waste from the biomass energy industry. The typical chemical composition of rice husk ash is 84.3% SiO_2, 12.2% loss on ignition, 1.4% CaO, 0.6% Fe_2O_3, 0.5% MgO, 0.4% Na_2O, 0.3% Al_2O_3, and 0.2% K_2O [2]. Therefore, the rice husk ash can potentially prepare them as support of catalysts because the main component is silica. Improving them for specific substances by surface modification is very helpful in increasing the catalytic activity. In the present study, the sulfonic acid group has been studied to functionalize the RHA to increase the catalytic activity in esterification. The modified surface characteristics of synthesized materials were characterized with XRD, FT-IR, N_2 adsorption-desorption measurement, and SEM. The synthesized adsorbents were evaluated for their performances in the esterification of PFAD with methanol to produce methyl ester for biodiesel production.

2. Material and Methods

2.1 Materials and reagents

Toluene, Ethanol, Hydrochloric acid, and methanol were purchased from RCL Labscan Limited. 3-mercaptopropyl trimethoxysilane (3-MPTMS) was purchased from Sigma Aldrich. Hydrogen peroxide, sulfuric acid, sodium chloride, and potassium hydroxide were commercial grade and obtained from QRëC^{TM}. All the above materials were used without further purification. Deionized water was used throughout this work.

2.2 Preparation of RHA and RHA-SO_3H

Rice husk was immersed in DI water, 1 M HCl for 4 h, at a 40 g husk/L ratio. The husks were washed repeatedly with DI water and then dried in an oven at 110 ◦C for 2 days. Samples of rice husks were converted into adsorbent-rice husk ash (RHA) by heat-treating using ceramic crucibles at 700 ◦C for 6 h in a muffle furnace. The heated rice husks were crushed to obtain an approximate diameter of < 2 mm. The sulfonic acid functionalized rice husk ash (RHA-SO_3H) was prepared by mixing 5 g of RHA with 41.66 ml of dried toluene. The mixture was refluxed for 2 h, and then 5 g of 3-MPTMS was slowly added by a dropper. The mixture was refluxed again for 48 hours. Finally, the material was filtered, washed with toluene and ethanol, and dried at 80 °C for 2 h. Relatively long oxidation times (24 h) and a sixfold excess of H_2O_2 are recommended to avoid disulfide contamination and to achieve the selective oxidation of the mercapto group into sulfonic acids. The solid material was further acidified with 0.05 M H_2SO_4 for 2 h to confirm that all the sulfonic groups were protonated. The solid material obtained was then filtered, washed with water several times, and dried in air at 80 °C for 24 h [3].

2.3 Characterization of catalyst

The structures of RHA and RHA-SO_3H materials were analyzed by powder X-ray diffraction (XRD). The XRD analysis was performed on a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation operated at 40 kV and 40 mA. The functional groups of these samples were analyzed FTIR. The FTIR spectra were obtained from a Spectrum 2000 FTIR spectrometer (Perkin-Elmer) with the usual KBr pellet method. The spectral range was chosen from 4000 to 400 cm^{-1}. The textural properties of the synthesis materials were analyzed by nitrogen (N_2) adsorption-desorption measurement at -196 ^oC on an Autosorb IQC-Quantrachome. All samples were pretreated at 150 ^oC for 2 h and then measured for exact weight before the adsorption. SEM analyzed the morphology of these adsorbents. The SEM analysis was carried out using a scanning electron microscope (Model JEOL JEM-2010) at an electron acceleration voltage of 20 kV. Before scanning, the samples were coated with a thin layer of gold using a sputter coater to make them conductive. The acid group level of the functionalized RHA was quantified by standard acid-base titration, where a known exact mass (0.1 g) of the sample was added to 15 ml of 2.0 M NaCl solution and allowed to equilibrate for 1 h. Then, it was titrated by the dropwise addition of 0.01 M NaOH. The acidity was calculated from Eq. (1).

$$N=\frac{CV}{W} \quad (1)$$

where N is the acidity (mmol g^{-1}), V is the volume of NaOH solution consumed in the titration (ml), and W is sample weight (mg).

2.4 Esterification study

Esterification of commercial PFAD (Morakot Industries Public Co., Ltd. (Thailand) with methanol was carried out in a 50-mL three-neck round-bottom flask equipped with a magnetic stirrer and a reflux system. The cooling water temperature (5°C) was controlled by bath circulating equipment. Before being used, the catalyst was dried at 100 °C for 2 h. The reaction temperatures were set at 100 °C using an oil bath. The operating parameters were the molar ratio of methanol: PFAD of 9:1, catalyst loading of 1 wt% (based on the PFAD weight), and reaction time of 1 h. The reaction mixture was analyzed for the free fatty acid (FFA) conversion using the acid-base titration method with 0.01 M NaOH and bromothymol blue as the indicator. The free fatty acid conversion was calculated from Eq. (2).

$$\text{Conversion (\%)} = \frac{\text{mole of FFA}_{\text{initial}} - \text{mole of FFA}_{\text{remain}}}{\text{mole of FFA}_{\text{initial}}} \times 100 \quad (2)$$

3. Results and discussion

3.1 Characterization of materials

X-ray patterns for RHA and RHA-SO_3H materials are presented in Fig.1. The XRD patterns of this material displayed a broad diffraction peak appearing in 2θ around 15-30 °, corresponding to the characteristic of silica in amorphous form. In addition, they observed a diffraction peak at 27 °, related to a characteristic of silica in quartz form. However, the RHA-SO_3H materials exhibited a lower XRD intensity than primary RHA due to the functionalization of the sulfonic acid on RHA surfaces, resulting in a disorder of silica structure.

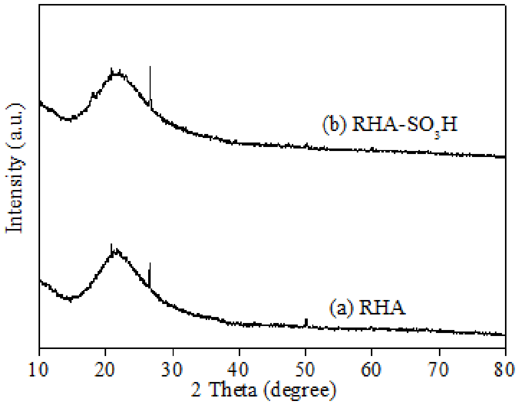

Fig. 1. XRD pattern of (a) RHA and (b) RHA-SO_3H

Qualitative identification of functional groups was accomplished by FT-IR spectroscopy. Fig. 2 shows the FT-IR spectrum of RHA and sulfonic acid functionalized RHA materials over the 4000-400 cm-1 range. A broad band in the range of 3700-3010 cm^{-1} was seen, which can be attributed to the framework of Si-OH group interaction with the defect sites and adsorbed water molecules. The Si-OH peak appeared at about 3142 cm^{-1}. The asymmetric stretching vibrations of Si-O-Si were observed by the absorption bands at 1110 cm^{-1}. The functionalized RHA with sulfonic acid groups (Fig.2b) shows a peak related to S=O stretching at 1228 cm^{-1} and C-H stretching of methyl groups at 3042 cm^{-1}. These results confirmed that the sulfonic acid functionalized on the RHA structure by replacing silanol groups, as seen in the synthesis pathway in Fig. 3.

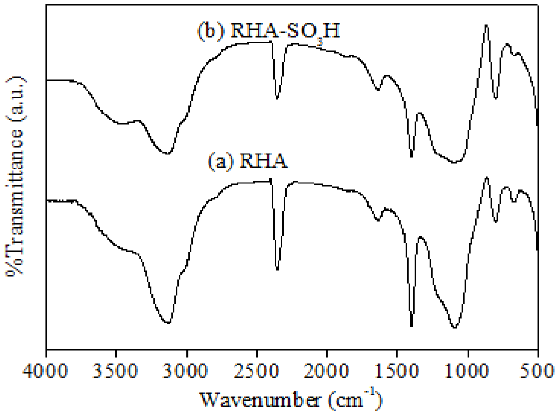

Fig. 2. FT-IR of (a) RHA and (b) RHA-SO_3H

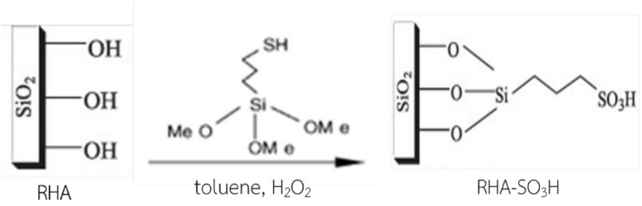

Fig. 3. Synthetic route for RHA-SO_3H.

The textural properties of RHA and RHA-SO_3H are summarized in Table 1. The RHA-SO_3H samples exhibited a lower specific surface area, pore volume, and diameter than RHA. Furthermore, the RHA-SO_3H determined the acid value as 0.55 mmol g-1 from acid-base titration. These results indicated that propyl sulfonic acid groups were functionalized on the RHA surface.

Table 1 Physicochemical and textural properties of RHA and RHA-SO_3H samples.

Sample	Specific surface area (m^2/g)	Pore volume (cm^3g^{-1})	Pore diameter (nm)	Acidity ($mmol\ g^{-1}$)
RHA	205	1.12	23.4	*n.d.*
RHA-SO_3H	193	0.98	21.2	0.55

SEM analyzed the surface morphology of RHA and RHA-SO3H. The micrographs in Fig. 4A represented the RHA surface. It revealed the accumulation of silica particles and the surface roughness. However, as seen in Fig. 4B, the morphology of RHA-SO_3H was not significantly different from that of pristine RHA.

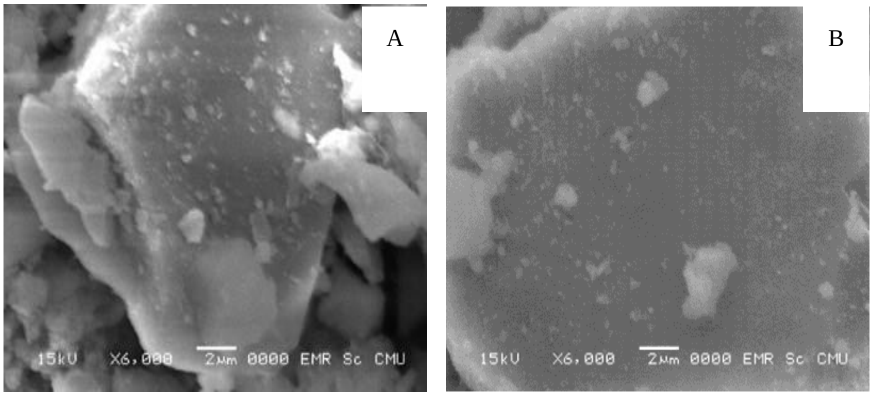

Fig 4. SEM image of (A) RHA and (B) RHA-SO_3H at a magnification of 6000x

3.2 Esterification of PFAD with methanol

The FFA content of the initial PFAD was 53.86% palmitic acid (C16:0), 44.49% oleic acid (C18:1), and 1.65% stearic acid (C18:0). The esterification of PFAD with methanol generated methyl palmitate, methyl oleate, and methyl stearate as desired fatty acid methyl ester (FAME) products. Figure 5 shows the percent conversion of PFAD in esterification with methanol. The RHA-SO_3H exhibited higher conversion (54.3 %) than without catalyst (5.1 %). The result indicated that the sulfonic acid group enhanced the catalytic activity to produce the methyl ester.

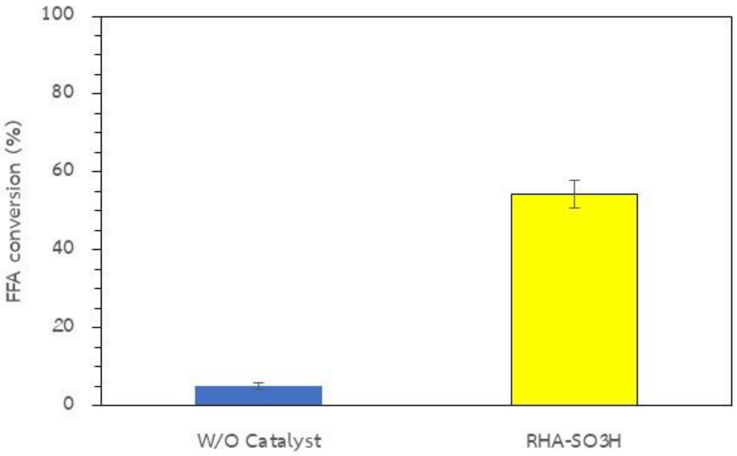

Fig. 5. Esterification of PFAD with methanol over RHA-SO_3H catalyst and without catalyst. Reaction conditions: catalyst loading, 1 wt%; molar ratio of PFAD: methanol, 1:9; time, 1 h; temperature, 100 °C.

4. Conclusion

The functionalized sulfonic acid rice husk ash was successfully prepared via the grafting method with 3-MPTMS**.** The RHA-SO_3H exhibited high acidity with mesoporosity. The enhanced acidity of RHA-SO_3H catalysts promoted the acid conversion in the esterification of free fatty acid with methanol. Further research is underway to investigate the potential use of the RHA-SO_3H as solid acid catalysts for biodiesel production.

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