

Development of Sulphonated Sago Pith Waste Catalyst for Esterification of Palm Fatty Acid Distillate to Methyl Ester

Zarifah Zailan, Hilman Ali, Jia Wen Chau, Mazura Jusoh, Muhammad Tahir, Zaki Yamani Zakaria*

School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia.

zakiyamani@utm.my

Biodiesel is considered as one of the renewable sources of energy that has been highlighted as an alternative fuel due to its versatile properties. Despite the fact that it is remarkable, there are several issues such as its industrial production cost and environmental concern related to the usage of homogenous catalyst. Among the alternatives are to switch to use Palm Fatty Acid Distillate (PFAD) as a low-cost feedstock and utilizing a heterogeneous Sago Pith Waste (SPW) catalyst. In this study, the heterogeneous catalyst was prepared by sulfonating the incomplete carbonized SPW under various preparation conditions. One factor at a time (OFAT) method was carried out to determine the optimum preparation condition for sulfonated SPW catalyst and the produced catalysts were characterized to study its morphology, crystallinity, surface area and acid density. The optimum preparation condition for sulfonated SPW catalyst were 1:20 ratio mass of dry SPW to the volume of sulfuric acid, 5 minute of sulfonation time and 200 °C of carbonization temperature. The optimum catalyst prepared gave 99.34 % methyl ester yield and 93.03 % PFAD conversion. Substantial yield and conversion obtained indicated the suitability of SPW as a heterogeneous catalyst for biodiesel production.

1. Introduction.

In order to achieve sustainable development, replacement for fossil fuel energy to a greener energy such as biodiesel in transportation sector is needed. The importance of these matter was reflected from EIA report in 2017 for United States of America, where the CO₂ gas emitted from transportation sector had exceed electric power sector CO₂ emission (Lee et al., 2018). As the amount of greenhouse gas released becomes a concern, the biodiesel production needs an urge for improvement. In a typical biodiesel production, virgin vegetable oil or animal fat is a prime source utilized as a feedstock which lead to a high biodiesel price. Palm Fatty Acid Distillate (PFAD) has been identified as a cheaper alternative biodiesel feedstock over palm oil as 3.25 % of PFAD is generated from one tonne of crude palm oil refining process (Abdul Kapor et al., 2017).

Over the last decade, heterogeneous catalysts are preferable to be used over homogeneous catalysts due to the simple separation process, reusable, and economical (Tang et al., 2018). Many problems arise as the classical solid acid catalysts have lost their place in inorganic synthesis due to six main limitations that are low surface area, poor porosity, leaching of active sites, low activity at a lower temperature, water sensitivity, and low thermal stability (Khurshid, 2014). Recently, development of carbon-based heterogeneous acid catalyst was reported to hold multiple advantages such as surface hydrophobicity, chemical inertness, structural diversity and mechanical stability (Niu et al., 2018). The heterogeneous acid catalyst was made up from incomplete carbonized biomass incorporated with SO₃H group and has gained attention due to being greener, low cost and suitable for esterification of low-grade oil with high FFA content (Lokman et al., 2016). The performance of these types of catalyst depends on the catalyst synthesis conditions such as sulfonation time, partial carbonization temperature and H₂SO₄ volume (Mhlanga et al., 2009).

In this work, a heterogeneous acid catalyst derived from Sago Pith Waste (SPW) will be prepared through microwave-assisted sulfonation for esterification of PFAD into methyl ester. SPW is a fibrous residue rich in sago starch after most of the starch have been extracted from the rasped pith of the sago palm (Singha and Thakur, 2008). Approximately 58 - 67 % of SPW consist of starch which later becomes carbon precursor for the prepared catalyst. The aim of this study is to develop sulfonated SPW catalyst for the esterification of

PFAD into methyl ester. The methyl ester was produced via esterification of PFAD using developed catalyst prepared at the various conditions. The effect of synthesis parameter on methyl ester yield and conversion was observed, together with the kinetic study. The developed catalysts were characterized using BET, FESEM, XRD, FTIR and NH_3 – TPD. The effect of the preparation condition and kinetic study are discussed. The sulfonated SPW catalyst is expected to be able to produce high methyl ester yield and PFAD conversion.

2. Methods and materials

2.1 Material

The starting materials used in this research include SPW, sulphuric acid, methanol and PFAD. SPW was collected from the Hup Moh factory in Batu Pahat. The sulphuric acid was purchased from ICHEM Solution Sdn Bhd, Taman Universiti, Johor, Malaysia. The PFAD feedstock was obtained from Mewaholeo Industries Sdn Bhd, Pasir Gudang, Johor, Malaysia. The methanol was attained from the chemical store at School of Chemical and Energy Engineering, Universiti Teknologi Malaysia.

2.2 Preparation of catalyst

The dry SPW was placed into an oven for 24 h at 105 °C for moisture removal. The carbonization step was carried out inside a furnace at a temperature 180 °C to 210 °C for 1 h to produce the partial carbonized SPW. The sulphonation step was carried out by mixing and stirring the mixture of 5 g of partial carbonized SPW with 60, 75, 90 and 100 mL of H_2SO_4 for 15 min. The mixture was placed into a microwave (Sharp R213C) for 3, 5, 7 and 9 min at power level 560 W, followed similar synthesis condition reported by Saimon et al. (2018). After cooling the sulfonated partial carbonized SPW catalyst, it was filtered and washed with excessive distilled water. To remove excessive sulphate ion on the catalyst, the sulfonated partial carbonized SPW was washed using hot distillate water. Then the catalyst was placed into an oven for 6 h at 100 °C for drying.

2.3 Catalyst characterization

X-Ray Diffraction (XRD), Brunauer-Emmet-Teller (BET), Field Emission Scanning Electron Microscopy (FESEM), Temperature-Programmed Desorption - Ammonia (NH_3 -TPD) and Fourier Transform Infrared (FTIR) techniques were performed to characterize the catalyst produced. FESEM (Quanta FEI 400F) was used to study the morphology of the catalyst produced. The functional group of the catalyst was determined through FTIR analysis using Shimadzu IRTracer-100. The crystallinity of the catalyst produced was measured within a scan range of $\theta=0^\circ$ - 100° at a scanning rate of 4° min^{-1} through XRD analysis (Bruker, D8 Advance). Acid site density of the catalyst was measured through TPD- NH_3 analysis by using Micromeritics AutoChem II.

2.4 Esterification procedure

The esterification of PFAD was carried out in the presence of the sulfonated SPW catalyst. In this regard, a magnetic stirrer and a 50 mL two-necked round bottom flask were coupled with the condenser in order to re-condense the evaporated methanol. Briefly, the mixture of the methanol, PFAD and catalyst was stirred at conditions such as catalyst concentration (2.5 wt%), methanol to oil molar ratio (10:1), reaction temperature 70 °C, and reaction time 90 min. After each reaction, the suspension was allowed to settle down for 30 min before being separated. At the end of each esterification reaction, titration method using potassium hydroxide was carried out to determine the acid value (AV) of methyl ester. The AV was calculated using Eq(1), methyl ester conversion was calculated by following Eq(2) and yield was calculated using Eq(3). The present of methyl ester in the biodiesel was verified by the gas chromatography equipped with flame ion detector (GC-FID) analysis.

$$\text{Acid Value (AV)} = \frac{N \times M_w \text{ KOH} \times \text{Volume of KOH used (ml)}}{\text{Mass of biodiesel (g)}} \times 10 \quad (1)$$

where N is normality of KOH used and M_w is molecular weight of KOH; 56.11 g/mol.

$$\text{Conversion (\%)} = \frac{\text{AV of PFAD} - \text{AV methyl ester}}{\text{AV of PFAD}} \times 100 \% \quad (2)$$

$$\text{Yield (\%)} = \frac{\text{Weight of Biodiesel}}{\text{Weight of PFAD}} \times 100 \% \quad (3)$$

3. Result

3.1 Catalyst characterisation

From Figure 1, the IR spectra illustrated three components which are the sulfonated SPW, partial carbonized SPW and dry SPW. IR spectra for partial carbonized SPW and dry SPW were similar at bands $3,300\text{ cm}^{-1}$, $2,900\text{ cm}^{-1}$ and $1,050\text{ cm}^{-1}$. The absorption at band $2,900\text{ cm}^{-1}$ was attributed to stretching of CH_2 group aliphatic (Putra et al., 2018). The band at $3,300\text{ cm}^{-1}$ was associated to $-\text{C}-\text{H}$ stretching mode of the bending alkene group, whereas the band at $1,050\text{ cm}^{-1}$ were associated with $\text{C}=\text{C}$ stretching mode of the mono-substituted alkene group. It should be noted that the peaks for the partial carbonized SPW and dry SPW were present with a weak intensity compared to the sulfonated SPW. This could be due to the efficient IR adsorption ability of the carbon frameworks that were rearranged from the high-temperature thermal treatment (Nakamura et al., 2007). For sulfonated SPW catalyst, the band at $3,585\text{ cm}^{-1}$ was attributed to $-\text{O}-\text{H}$ stretching mode of alcohol group (Saimon et al., 2017). The successfulness of sulfonation in introducing sulfonic group onto the SPW surface area was confirmed by the presence of strong absorption band occurred at $1,033\text{ cm}^{-1}$ and $1,147\text{ cm}^{-1}$, indicating the existing of sulfoxide group ($\text{S}=\text{O}$) and thiocarbonyl group ($\text{C}=\text{S}$) in sulfonated SPW catalyst.

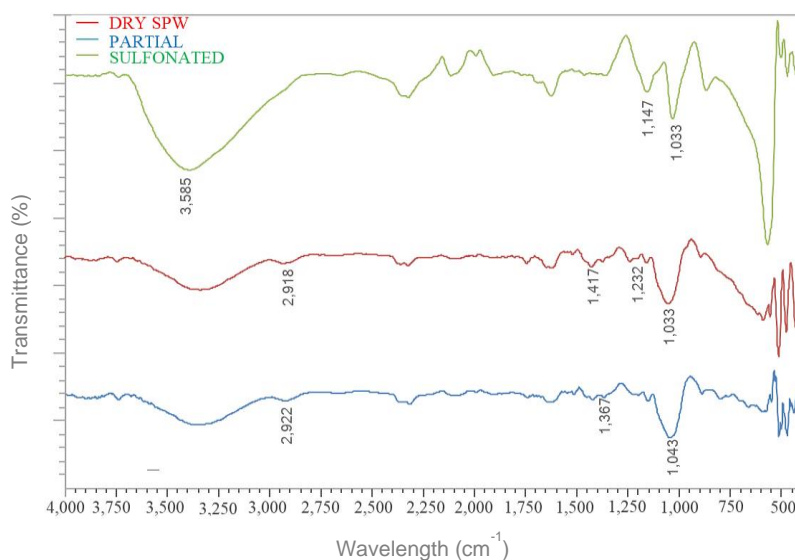


Figure 1: FTIR analysis for raw SPW, partial carbonized SPW and sulfonated SPW

Figure 2a shows both partial carbonized SPW and raw SPW exhibited similar diffraction peak. The broaden peaks were obtained from the XRD plot at $2\theta = 15 - 30^\circ$ and a weak peak at $2\theta = 35 - 50^\circ$. Both peaks indicated the existing of amorphous carbon consisted of aromatic carbon sheet oriented at a random fashion (Saimon et al., 2017). The X-ray diffraction intensity peaks were lower for post-sulfonation process indicated a smaller crystal size had caused by destruction effect of the physical and chemical structure of SPW which is in accordance with BET and FESEM result. The average size of the catalyst crystal calculated from the two peaks at $2\theta = 17.45^\circ$ and 22.51° was 1.69 nm.

From Figure 2b, there were three unique peaks related to sulfonated SPW, partial carbonized SPW and dry SPW that were revealed in the NH_3 -TPD plot. Sulfonated SPW had its peak at around 580°C in the range of 380°C to 900°C . The existence of the sulfonic groups around $500 - 700^\circ\text{C}$ evidenced the presence of strong Brønsted acids on the catalyst active site. The peak for dry SPW and partial SPW are almost similar at in the range of 200°C to 400°C and 240°C to 500°C . This illustrated the presence of the carboxyl groups (around $400 - 550^\circ\text{C}$) which explained the presence of weak Brønsted acids on the catalyst active site. Typically, acidic groups can be classified into three major groups including phenolic ($-\text{OH}$), carboxylic ($-\text{COOH}$) and sulfonic ($-\text{SO}_3\text{H}$). Among these three, only the sulfonic group has sufficient acid strength to participate in the esterification of PFAD.

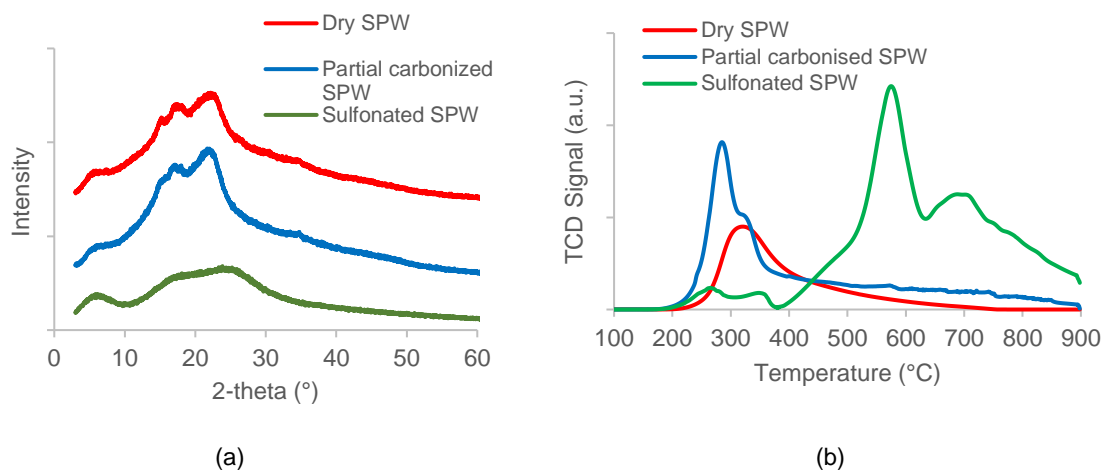


Figure 2: Analysis for raw SPW, partial carbonized SPW and sulfonated SPW (a) XRD, (b) NH₃ - TPD

From the BET result, it was observed that the surface area increased from partial carbonization of dry SPW until sulfonation process from $4.445 \text{ m}^2\text{g}^{-1}$ to $11.097 \text{ m}^2\text{g}^{-1}$. A high specific surface area of $11.097 \text{ m}^2\text{g}^{-1}$ was obtained indicated that most of the SO_3H group were in the interior part of the catalyst, enabling the reactants to bond with more acid sites, and thus ensuring a better catalytic activity. Basically, the BET surface area depends on the structural feature of the composition (Jiang et al., 2010). It was believed that a higher concentration of the support element led to the breaking of the dry SPW phase. This phenomenon caused a simultaneous increase in the surface area and reduction of the pore diameter. From the BET result, it was proven that sulfonation greatly influenced the porosity of SPW whereby the reduction of pore volume from 0.015 to $0.013 \text{ cm}^3\text{g}^{-1}$ and the average pore radius from $1,458 \text{ nm}$ to 432 nm .

Figure 3 shows the FESEM images for partial carbonized SPW and sulfonated SPW at 600x magnification. The FESEM image shows that the partial carbonized SPW had uneven distribution of carbon shell and many irregular pores that could function well as the active sites of the catalyst. The image of sulfonated SPW (Figure 3b) revealed that the size of the particles and pores of the catalyst decreased due to the acid treatment during the sulfonation process.

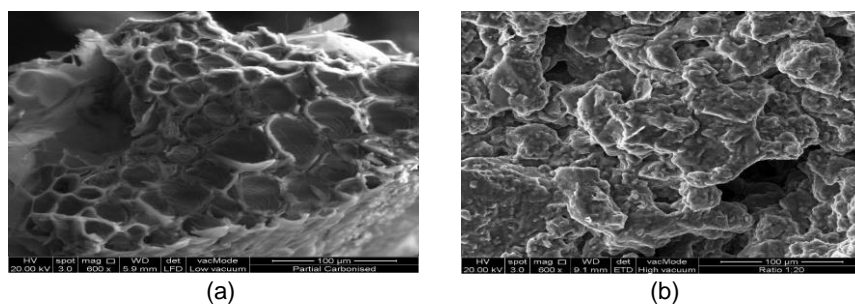


Figure 3: FESEM images at 600x magnification (a) partial carbonized SPW, (b) sulfonated SPW

3.2 Effect of synthesis parameter on catalytic performance

3.2.1 Effect of partial carbonization temperature

The carbonization temperature is one of the important parameters in catalyst synthesis as it is able to influence the carbon form structure and amount of oxygen content in carbon matrix of carbonaceous material, thus indirectly affect catalyst acid density. For this study, the sulfonated SPW catalyst was prepared by altering the partial carbonization temperature within the range of $180 - 210 \text{ }^\circ\text{C}$ as shown Figure 4a with other conditions fixed (5 g of dry SPW, ratio of mass of partial carbonized SPW to volume of sulphuric acid of 1:5 and sulfonation time of 5 min). From Figure 4a, biodiesel yield was only 93.61 % at $180 \text{ }^\circ\text{C}$ which was substantially increased to 96.95 % by increasing the operating temperature to $200 \text{ }^\circ\text{C}$. It was clearly found that FAME conversion was reduced from 94.23 % to 91.24 % over reaction temperature $200 \text{ }^\circ\text{C}$ and $210 \text{ }^\circ\text{C}$. The increase of carbonization time may help to eliminate $-\text{OH}$ and $-\text{COOH}$ group in SPW but an excessive carbonization was not favourable for new acid site introduction due to its rigid structure (Ning and Niu., 2017)

and may lead to a drop of catalyst catalytic performance. By drawing on the results, the optimum reaction temperature for the esterification of PFAD was found to be 200 °C with a yield of 94.23 %.

3.2.2 Effect of ratio of sulfuric acid to partial carbonized SPW mass weight

The ratio of mass of partial carbonized SPW to the volume of H₂SO₄ is one of the essential factors to find the optimum condition for catalyst synthesis. The catalyst synthesis conditions were 5 g of dry SPW, partial carbonization temperature 200 °C and sulfonation time 5 min. As can be seen Figure 4b, by increasing the ratio from 1:5 to 1:20, biodiesel yield increased gradually from 84.42 % to 99.34 %. By increasing the ratio up to 1:20, biodiesel yield increased due to greater amount of polymeric attachment of the sulfonate groups (-SO₃H) on the surface of the catalyst. This highly increased the level of the acid strength in the active site due to covalent attachment of the SO₃H groups to the active sites. This phenomenon increases the catalyst activity of the catalyst, thus consequently improves both the percentage yield and conversion of the reaction up to 99.34 % and 94.03 % at a ratio of 1:20.

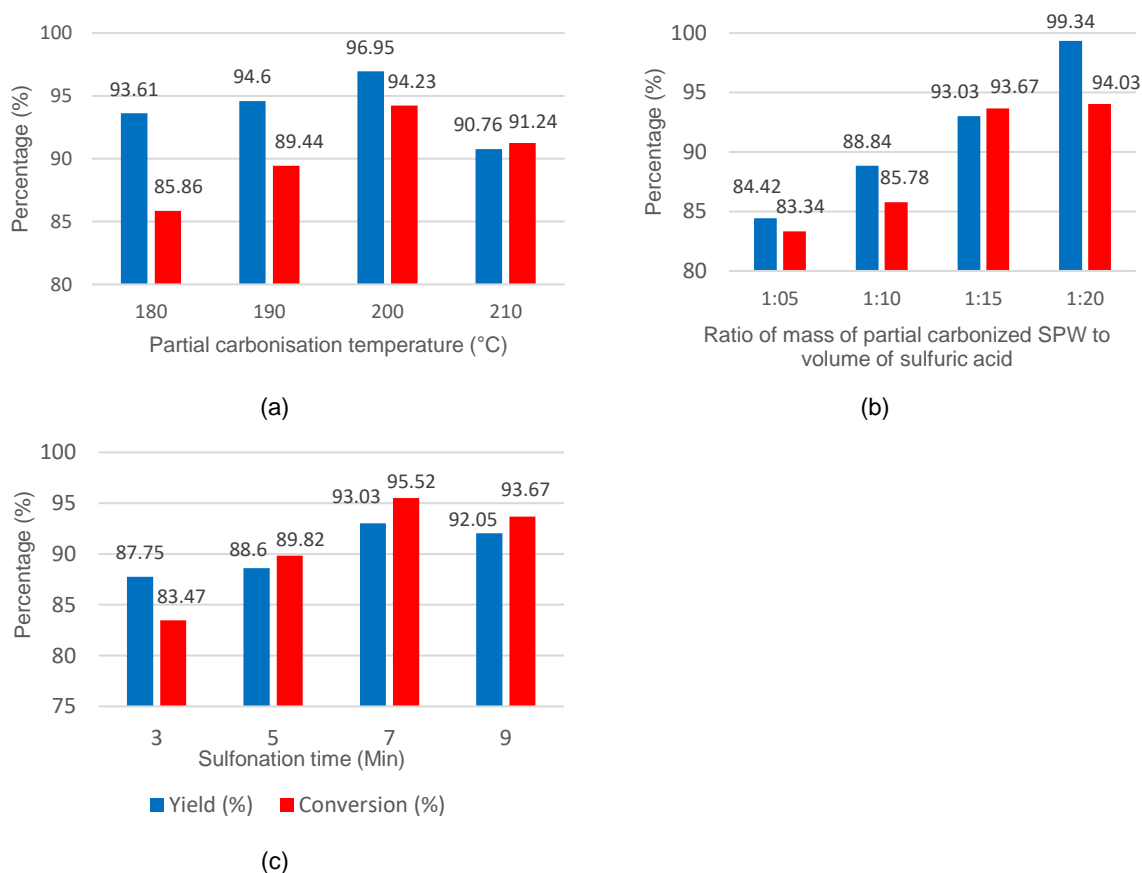


Figure 4: Effect of different parameter (a) partial carbonization temperature, (b) ratio of mass of partial carbonization SPW to sulphuric acid volume (c) sulfonation time

3.2.3 Effect of sulfonation time

To study effect of sulfonation time, the esterification conditions were standardized at a temperature 70 °C, reaction time 90 min and catalyst loading 2.5 wt%. The catalyst synthesis conditions were 5 g of dry SPW, partial carbonization temperature 200 °C and ratio of mass of partial carbonized SPW to volume of sulphuric acid 1:5. Figure 4c shows the effect of sulfonation time between 3-9 min. As the sulfonation time increases from 3 and 5 min, the yield of methyl ester was enhanced from 93.672 % to 95.524 %. The yield then started to decrease after extending of the sulfonation time beyond 5 min. During sulfonation process, a certain period was needed to ensure SO₃H group was able to attach onto the catalyst surface area. A great structure destruction caused by longer sulfonation time may lead to poor sulfonate group distribution, thus bringing to a lower methyl ester yield (Sandouqa et al., 2019). From the results, the highest yield was achieved at 5 min of sulfonation time during the synthesis of the catalyst.

3.3 Kinetic study

The kinetic study was carried out at three different temperatures 50 °C, 60 °C and 70 °C with a fixed catalyst loading at 2.5 wt% and 1:10 ratio methanol to PFAD. In this study, the trend of reaction rate constants increases with reaction temperature, with the lowest and highest reaction rate constants observed at 50 °C and 70 °C. It is assumed that the process undergoes a pseudo-first order reaction kinetic. From the experiment, it was found that the activation energy (E_a) was 173.305 kJmol⁻¹K⁻¹. These high values for the activation energy indicate that the reaction is temperature-sensitive and therefore, the result confirms that the process is a kinetically controlled reaction.

4. Conclusions

In this research, sulfonated SPW was successfully synthesized by using optimum condition of mass of dry SPW 5 g, partial carbonization temperature 200 °C, 1:20 ratio mass of partial carbonized SPW to volume of H₂SO₄, and 5 minutes sulfonation time. These optimum conditions were able to produce highest yield at 99.34 % and conversion at 94.03 %. The results showed that the –SO₃H from sulphuric acid strongly supports the catalyst structure of the sulfonated SPW. It can be concluded that partial carbonized SPW treatment with H₂SO₄ has tremendous potential to be an excellent catalyst that could directly esterify high fatty acid feedstock such as PFAD to yield high methyl ester.

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