Synthesis of Solid Catalyst from Palm Empty Fruit Bunch for Production of Biodiesel through Esterification

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Abstract. Application of solid acid catalyst in biodiesel production gains much attention from researchers as it is suitable for most of the non-edible and low value oils which will significantly cut down the total production cost and reduce corrosion issue. In this research, biomass from palm empty fruit bunch is used as the carbon precursor to synthesis activated carbon (AC) before sulfonated by 4-benzenediazonium sulfonate (4-BDS) to produce solid acid catalyst. The synthesized catalysts were characterized and the performances were tested in esterification of palm fatty acid distillate (PFAD) to produce biodiesel. Scanning Electron Microscope (SEM) showed that a clear porous and rough surface was developed after calcination at relative low temperature (200 °C) which favors the attachment of the acid active site. It also found that that the total acid sites of the catalyst increased when sulfanilic acid loading increased during sulfonation. In catalytic activity test, the result showed that catalyst calcined at 200 °C and catalyst sulfonated with 15:1 sulfanilic acid to AC ratio was the optimum catalyst as they gave the highest biodiesel yield at 73.14%.

1. Introduction

Currently, the most common catalyst technologies used are homogeneous sodium methyleate or sulfuric acid catalyst as they are easily available, cheap and little issues with supply. Besides, since the catalyst is working in same phase as the reactants, handling all materials in liquid state is much easier. Homogeneous catalyst is also able to achieve high conversion rate within a short period as compare to heterogeneous catalyst. However, the issues such as sensitive to high free fatty acid (FFA) feedstock, soap formation, yield losses and high cost of separation and purification always occur in homogeneous alkaline catalyzed reaction [1, 2]. For the case of homogeneous acid catalyst, although it is insensitive to high FFA feedstock and able to avoid soap formation, this catalyst technology however still difficult to be recycled, causes corrosion problem and requires higher reaction temperature [2]. To overcome the drawbacks of homogeneous catalyst usage in biodiesel production, this study suggested to synthesis heterogeneous acid catalyst from biomass as acid catalyst is suitable for high FFA feedstock which is cheaper and solid catalyst is easy to be separated hence potentially reduces overall production cost. Commonly, direct synthesis method of activated carbon from biomass is the simplest and environmental friendly whereby the biomass is calcined under controlled temperature and controlled atmosphere or without presence of air. This method able to produce highly expanded mesoporous surface from low surface carbon precursor [3]. When the calcination temperature was too high, the carbon structure of the biomass
experienced thermal decomposition which reduced the SO$_3$H groups attachment during sulfonation [4, 5]. The synthesized activated carbon obtained from biomass can be acid functionalized whereby the active part of the catalysts is attached. Current research will focus on sulfonation by using 4-BDS method as it was reported by number of researches that 4-BDS sulfonation method outperformed in terms of catalytic stability and contribute to high conversion of FFA in esterification [6, 7]. It was found that the catalytic activities of the catalyst sulfonated by using 4-BDS method was comparable or even higher than Amberlyst-15 even though SO$_3$H density on it was lower than Amberlyst-15 [7, 8]. Besides, the researchers also suggested that sulfonation by 4-BDS was a more effective sulfonating method for carbon materials with aromatized or graphitic structure [6]. High stability of covalent C-PhSO$_3$H bonds in spent catalyst sulfonated by using 4-BDS method also supporting the high reusability [9]. However, the optimum synthesis conditions of 4-BDS method was still relatively unexplored particularly towards its effect in biodiesel production. In this study, the effect of calcination temperature and 4-BDS sulfonating agent amount was investigated on the carbon precursor palm empty fruit bunch (EFB) for biodiesel production from palm fatty acid distillate (PFAD) which is a high FFA content feedstock. After preparation and treatment of solid catalyst, the characteristics of catalyst such as surface morphology of catalyst and density of sulfonic acid were analyzed.

2. Materials and methods

2.1. Materials

Palm empty fruit bunch collected from oil palm estate in Malaysia, hydrochloric acid (35%), sulfanilic acid (99%), sodium nitrite (98%), phosphoric acid (30-32%), methanol (99.9%), potassium hydroxide (99%), n-hexane (99%) and isopropanol (99.9%) were purchased from Merck, Malaysia. PFAD was collected from a local palm oil refinery industry. Gas chromatography (GC) external standard references for methyl esters include methyl palmitate (99%), methyl stearate (99%), methyl oleate (99%) and methyl linoleate (99%) were purchased from Sigma-Aldrich, Malaysia.

2.2. Synthesizing catalyst from palm empty fruit bunch and sulfonation by arylation of 4-benzenediazonium sulfonate

EFB biomass was impregnated with 30 % phosphoric acid in weight ratio of 7:1 for 24 h. Then, it was carbonised in a furnace at different temperature for 2.5 h. The AC calcined at 200°C to 600°C was named as AC200, AC300, AC400, AC500 and AC600 respectively. The sulfonation procedure was done based on the modification of the experimental work from [6]. 15 g of sulfanilic acid was dispersed in 1 M HCl aqueous solution in a round bottom flask. The temperature of the flask was maintained at 5°C in ice water bath with continuous stirring. 1 M NaNO$_2$ aqueous solution was added dropwise. The mixture in the flask was allowed to settle down and white precipitate of 4-BDS formed was filtered off, washed with deionised water and weighed. 4-BDS precipitate was then mixed with deionised water and ethanol in a 500 mL beaker. Activated carbon was added into the beaker and maintained the temperature at 3 – 5°C. Subsequently, 30 – 32% H$_3$PO$_4$ was added and stirred for 30 min. The resulting sulfonated AC was filtered, washed and dried in the vacuum overnight. The procedure was repeated by using AC with different calcination temperatures and also different sulfanilic acid to AC weight ratios.

2.3. Esterification reaction

The solid acid catalyst synthesised was then used to test its catalytic performance in esterification of PFAD to produce biodiesel. The reaction was performed in a 250 mL round bottom flask equipped with a magnetic stirrer and oil bath at 110°C. 5 wt% of catalyst was added to reaction mixture with 10 g PFAD and methanol with molar ratio to oil of 30. The reaction was allowed to run for 4 h at 350 rpm stirring speed. After the reaction, the excess methanol was removed by evaporation and
the weight of the product was recorded. The procedure was repeated for various parameters as shown in Table 1.

| Parameters                              | Variables                          |
|----------------------------------------|------------------------------------|
| Different calcination temperature catalyst | CAT200, CAT300, CAT400, CAT500, CAT600 |
| Different sulfanilic acid weight ratio catalyst | CAT0.5:1, CAT1:1, CAT5:1, CAT10:1, CAT15:1 |

2.4. Catalyst characterizations

The synthesized catalyst was subjected to Scanning Electron Microscope (SEM) under 20.0 kV at 500 and 2000 magnification, Energy Dispersive X-ray (EDX), surface analysis using Brunauer-Emmett-Teller (BET) method and total acid density test through back titration with sodium hydroxide (NaOH).

2.5. Product characterization

The biodiesel samples produced were tested with gas chromatography (GC) (Perkin Elmer) by injecting and vaporising the sample into the head of the chromatography column and allow the inert gas flow through the column. Vaporisation and separation of sample mixture into individual component in GC enable the components in the biodiesel sample can be quantitatively measured. GC was operated at injector temperature of 250 °C, split flow ratio of 50:1, carrier gas at 24.7 psi, helium flow through column at 2 mL/min and flame ionization temperature of 270 °C. The GC peak areas obtained from the analysis were compared with the methyl ester standard calibration curves to calculate the biodiesel concentration and yield. The weight and yield of biodiesel can be calculated by using Eq.1 and Eq.2.

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\text{Actual Weight of Methyl Ester Produced (g)} = \frac{\text{concentration of methyl ester, g/L}}{\text{Dilution Factor, g/L}} \times \text{Weight of reaction product, g}
\]  
\[
\text{Biodiesel Yield (%)} = \frac{\text{Actual Weight of Methyl Ester Produced, g}}{\text{Theoretical Weight of Methyl Ester Produced, g}} \times 100\%
\]

3. Results and discussion

3.1. Catalyst characterizations

Based on the images shown by SEM in Fig 1(a), raw palm EFB naturally had a tough lignocellulosic structure. The surface of the raw EFB was dense and consisted less cracks and crevices that were available for acid sites adsorption. As comparison with raw EFB, a phosphoric acid activated and calcined activated carbon (AC) had a clear pore structure development whereby all AC calcined at different temperatures exhibited a rough texture surface. The activating agent phosphoric acid and calcination allowed the development of mesoporous structure. Noted that in Fig 1(b), AC200 has a very well defined mesoporous structure and this gave a high surface area capacity for acid adsorption. As the calcination temperature increased as shown in Fig 1(c) and Fig 1(d), the structure of AC became more irregular, loose, more flakes appeared and ladder shape structure formed.
The elements present in the raw EFB, activated carbons and sulfonated activated carbons from EDX analysis are shown in Table 2. Note that the raw EFB consisted of magnesium and calcium mineral which might possibly gained from their contact with soil during harvesting and transportation itself. It showed that magnesium and calcium mineral are completely removed after pre-treatment of phosphoric acid, water washing and calcination. According to the study by [10], these mineral elements can be removed by using mild acid leaching and water washing treatment which explained the EDX result in Table 2. Table 2 also shows that all catalysts had sulfur content (S) increased after sulfonation which indicated the successful attachment of sulfonic group on AC. For catalyst calcined at different temperatures, CAT200 showed the highest S content which is 3.52% from other calcination temperatures. For catalyst sulfonated with different amount of sulfanilic acid, CAT15:1 showed the highest S content 15.98%. Hence, based on the previous interpretation, CAT200 was predicted to have better sulfonic group attachment and 15:1 was the optimum sulfanilic acid to AC sulfonation ratio.

| Sample     | C%   | O%   | Mg% | Ca%   | Si% | P%  | S%  |
|------------|------|------|-----|-------|-----|-----|-----|
| Raw EFB    | 14.24| 54.21| 12.56| 18.99 | 0   | 0   | 0   |
| AC200      | 20.87| 29.40| 0   | 0     | 11.80| 37.93| 0   |
| CAT200     | 64.01| 32.47| 0   | 0     | 0   | 0   | 3.52|
| CAT15:1    | 46.24| 25.53| 0   | 0     | 4.22| 8.03| 15.98|

According to Fig 2a, the total acid density of the catalyst of CAT200 and CAT300 were similar and it decreased as the calcination temperature increased from 200 °C to 500 °C. However, at 600 °C calcination temperature, the total acid density bounced back to 2.36 mmol/g NaOH and this mostly related to the structure of CAT600. CAT600 which was flakier compare to other catalysts caused its existing acid sites were exposed directly to the NaOH solution while the acid sites of the other catalysts might trapped within the pores hence not easy to react with NaOH within the same time. In the case of sulfonation by using different sulfanilic acid to AC ratio, Fig 2b shows the total acid density of catalysts increased as the ratio increased. For CAT0.5:1 and CAT1:1 show almost similar and lowest total acid density which was 1.76 mmol/g and 2 mmol/g while CAT15:1 exhibited the highest total density among all which was 3.93 mmol/g and this result was supported by previous EDX anlaysis. Comparing the result of CAT15:1 with [6] who used the similar
procedure and sulfonation method, their catalyst only had 2.032 mmol/g of total acid density, this difference was most probably due to different carbon precursor was used caused the acid sites attached differently.

**Figure 2.** Effect of a) Calcination temperature and b) Sulfanilic acid to AC Weight Ratio towards total acid density of catalyst (Other sulfonation conditions: 5:1 sulfanilic acid to AC weight ratio, 1.5 h sulfonation duration, 3 – 5 °C sulfonation temperature, 200 C calcination temperature)

AC300 and CAT300 were selected as the samples to study the specific surface area of AC and catalyst. The sample before sulfonation (AC300) had the specific surface area of 5.6771 m$^2$/g and after sulfonation (CAT300) it reduced to 2.85067 m$^2$/g. Comparing to [9] using oil cake waste and [7] using conventional activated carbon as carbon precursor with same sulfonation method, the specific surface area of AC and catalyst in this study were much lower. [9] reported 777 m$^2$/g before sulfonation and 696 m$^2$/g after sulfonation while [7] reported 751 m$^2$/g before sulfonation and 602 m$^2$/g after sulfonation. Such as big difference between current research and literatures was most probably due to the different carbon precursor were used as the pores and surface development of activated carbon also depended on the original carbon material itself. However, both of the current research and literatures showed a reduction of specific surface area after sulfonation.

### 3.2. Esterification Process Study

CAT200, CAT300, CAT400, CAT500 and CAT600 were used to study the effect of catalyst calcination temperature on biodiesel yield and their relationship is shown in Fig 3a. CAT200 had the highest biodiesel yield which was 67.53%. This result is tally with the trend of the previous elemental analysis in Table 2 whereby the higher S content indicated higher chances of sulfonic group attachment on the catalyst hence more active sites were available to catalyse the reaction. CAT200 had the highest catalytic activity was most probably due to incomplete carbonisation at lower temperature. At 200 °C, the biomass dehydrated and developed the amorphous mesoporous surface without complete destruction of carbon structure but sufficient to remove wax and pectin on the raw EFB. At extreme high temperature, the pores of biomass will become compact due to sintering effect hence reduce the sulfonic group attachment. The effect of sulfanilic acid loading during sulfonation on the biodiesel yield and their relationship is shown in Fig 3b. CAT0.5:1 that sulfonated with less sulfanilic acid contributed the lowest biodiesel yield which is 8.29% followed by CAT1:1 12.62%. CAT5:1 and CAT10:1 showed almost similar biodiesel yield 42.75% and 43.72% indicated that when sulfanilic acid ratio increase from 5 to 10 did not have significant effect on the catalyst performance. As sulfanilic acid to AC ratio increase to 15:1 during sulfonation, a sharp improvement was observed in biodiesel yield which was 73.14%. This result
can be proven by previous catalyst characterization which showed CAT15:1 was the potential high performance catalyst.

![Figure 3. Effect of a) Calcination temperature and b) Sulfanilic acid to AC weight ratio towards biodiesel yield (Esterification conditions: 5wt% catalyst, 10 g PFAD, 30:1 methanol to oil molar ratio, 110°C reaction temperature, 4 h reaction duration)](image)

4. Conclusions
Palm empty fruit bunch (EFB) biomass was used as carbon precursor to synthesis activated carbon and then sulfonate through 4-benzenediazonium sulfonate (4-BDS) arlyration. SEM analysis showed a clear porous and rough surface was developed after calcination. EDX result showed that CAT200 had the highest sulfur content as compare to other catalysts calcined at higher temperature. EDX also showed that CAT15:1 had the highest sulfur content among all catalyst. As for total acid density test, CAT200 and CAT15:1 showed the highest acid attachment which was tally with the result of elemental analysis. Catalytic activity of catalyst calcined at different temperature and sulfonated with different sulfanilic acid loading were also tested through esterification of PFAD. The result showed that CAT200 was the optimum catalyst as it gave the highest biodiesel yield compared to other catalyst calcined at different temperatures. CAT15:1 also reported to have highest biodiesel yield which is 73.14% compare to other catalyst sulfonated with lower sulfanilic acid ratio. This study showed that the usage of EFB as heterogeneous catalyst in esterification of PFAD was promising and other synthesis conditions should also be explored in future studies for establishing a more cost-effective and sustainable catalytic pathway for commercial biodiesel production pathway.

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