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Green Synthesis of Sulfonated Activated Carbon from Palm Kernel Shell as Potential Catalyst for Hydrolysis of Palm Bunch Cellulose

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ABSTRACT

Biofuels are currently attracting attention as an alternative solution to the issue of depleting petroleum reserves and environmental problems. Biofuels can be produced through the catalytic conversion of biomass. Sulfonated activated carbon (SAC) is an active catalyst for biomass conversion. Sulfonated activated carbon is one of the green catalysts that has been successfully synthesized from palm shell waste. The SAC catalysts were prepared from palm shell waste by converting to activated carbon followed by sulfonating step. The SAC catalysts were characterized by using XRD, SEM, FTIR, and gravimetric methods. The SAC catalysts show as porous amorphous materials and have acidic properties, a prerequisite for good catalytic activity. Preliminary catalytic tests showed that the SAC catalysts can be used for the hydrolysis of cellulose from palm bunch waste which was shown by the existence of reducing sugar in the liquid product of hydrolysis.

1. Introduction

Biomass is the most abundant source of cellulose and could become an alternative to fossil resources for the sustainable production of chemicals and fuels. Many types of research have previously focused on the degradation of cellulose through some approaches, such as dilute acids, enzymes, and supercritical reactions. Principally, cellulose conversion into chemicals and/or fuels occurs through depolymerization reactions in acidic conditions with homogenous catalysts, enzymes, and subcritical and supercritical water [1]. Based on the literature, the major drawbacks of these methods include corrosion hazards, difficulties in separation from the mixture, control of enzymes, danger to the operator, and harsh reaction condition. Therefore, alternative catalysts are needed to overcome these issues. Several catalysts such as SAC, Al_2O_3, H-mordenite, HZSM-5, H-Beta, sulfated zirconia, and Amberlyst 15 have been used to hydrolyze cellulose into simple sugar [1],[6]. Among these catalysts, the SAC catalysts show the highest catalytic activity of about 70% conversion [6].

The SAC could be synthesized from biomass resources such as coconut shells, coffee residue, coal, rice husk and straw, corncob, bamboo, chitosan, etc. [2]-[5]. So far, there have been only a few reports on using palm kernel shells to synthesize SAC catalysts. The utilization of palm plantation industrial waste in the form of empty fruit bunches and abundant palm kernel shells as raw material for preparing carbon-based catalysts. It was known that palm kernel shells could be used as a raw material for synthesizing sulfonated activated carbon catalysts. Biomass waste material has been used as a carbon precursor for preparing solid acid catalysts such as activated carbon [10] through the carbonization and activation processes. Due to the low catalytic performance of activated carbon for the hydrolysis of cellulose to simple sugar, so the sulfonation process is needed to improve the acidity and, at the same time, enhance the catalytic activity. The sulfonation is the process of attaching the sulfonate ($–SO_3H$) group onto the activated carbon surfaces. The sulfonation process can be performed in mild conditions, is easy to handle, is inexpensive, and can be applied in various solid catalysts [10]-[12].

As mentioned above, the SAC catalysts can be prepared from the palm kernel shell through the simple sulfonation process. This work tries to synthesize and characterize the SAC catalysts from palm kernel shells and preliminary test the cellulose hydrolysis from palm bunches. Some parameters, such as crystallinity and morphology acid properties to identify the SAC catalyst's properties. In addition, the Fehling test is also performed to identify the simple sugar as a product of cellulose hydrolysis.

2. Research Methodology

2.1. Materials

Raw materials used in the research are palm kernel shells and palm bunch cellulose obtained from a palm oil industry in Bengkulu. For the activation, $ZnCl_2$ was used (Merck, Germany); for the sulfonation, H_2SO_4 was used 98% (BASF, Germany).

2.2. Procedures

1) Palm shell preparation

Palm kernel shells were collected from the waste of crude palm oil (CPO) factory in Bengkulu Indonesia. Palm kernel shells were separated from the waste mixture by soaking them in water and were then washed with water and dried in an oven at 110 ^oC for 4 hours. The dried palm kernel shells were ground into small pieces, then carbonized in a furnace at a temperature of 350 ^oC for about 2 hours to become charcoal. After the material reached room temperature, the obtained charcoal was milled into powder and sieved by 90 mesh. This dried charcoal powder was used as raw material to produce activated carbon (AC).

2) Synthesis of sulfonated activated carbon (SAC)

The SAC catalyst was synthesized in two steps, including the synthesis of activated carbon from palm kernel shells and the sulfonation steps, adopting the modified previous methods [2]-[5]. In the first step, the activation of charcoal was performed by the physio-chemical method. Charcoal powder was mixed into 0.1 M zinc chloride solution with a ratio of 1:10 (w/v). The mixture was then soaked, heated at 90 ^oC, and stirred with a hot plate magnetic stirrer at medium speed for 1 hour. The solid charcoal was separated from the mixture by filtration and washed twice with distilled water. The obtained solid charcoal was heated in an oven at 110 ^oC for 2 hours and was followed by heating at 300 ^oC for 2 hours to produce AC.

In the second step, the sulfonation process was carried out by mixing 90 mesh AC powder into various concentrated sulfuric acid solutions with a ratio of 1:5 (w/v). The sulfuric acid was prepared in various concentrations of 60%, 80%, and 98%, respectively. The mixture was heated at 120 ^oC and stirred with a hot plate magnetic stirrer for 2 hours. The solids were separated from the mixture by vacuum filtration and washed with distilled water until the pH of the filtrate was neutral. Then, the filtrate was heated in an oven at 70 ^oC for 12 hours to produce SAC. Three types of obtained catalysts were then signed as SAC 60, SAC 80, and SAC 98.

3) Characterization of sulfonated activated carbon (SAC)

The characterization of AC, SAC 60, SAC, 80, and SAC 98 catalysts was carried out to analyze the crystal phase, morphology, and acidity properties. The crystalline phase was analyzed by using a Philips D2 Phaser x-ray diffractometer at a diffraction angle range of 10 – 80^o of 2θ. The catalyst surfaces' morphology was imaged using scanning electron microscopy (Hitachi Flex-SEM 100). The acidity of the catalysts was determined gravimetrically by using ammonia adsorption, while the acid sites and $–SO_3H$ group were analyzed by a Fourier transform infrared (FTIR) spectroscopy (Shimadzu IR-Prestige 21).

4) Preliminary catalytic test in the hydrolysis of cellulose

Empty palm bunches of waste (EPBW) were collected from a CPO factory in Bengkulu Indonesia. The pre-treatment process of EPBW includes washing, drying, cutting, and grinding. The obtained powder was then sieved by 90 mesh to produce the powder of raw material of cellulose. For the delignification process, the powder of cellulose raw material was immersed in a 10% KOH solution for 24 hours. The mixture was heated in an autoclave at 110 °C for 4 hours. Then, the mixture was filtered by using a vacuum filter and washed with distilled water repeatedly until the pH of the filtrate was neutral. The obtained solid material is raw cellulose for catalytic tests.

To ease the hydrolysis process, the destruction of crude cellulose was carried out by immersion in an ionic liquid of 1-buty-3-methylimidazolium chloride (BMIMCl) with a ratio of 1:10 (w/w) [7]. The mixture was heated at 110 °C and stirred at medium speed on the hot plate stirrer for 60 minutes. After the mixture was cooled at room temperature, a total of 5 ml of distilled water was added to the mixture and was then centrifuged at 2500 rpm for 10 minutes. The supernatant was separated from the pellet and removed. The pellet was added 40 ml of distilled water and was centrifuged again at 2500 rpm for 15 minutes. The pellet was separated from the supernatant and used for further experiments on the hydrolysis test of cellulose.

The catalyst tests for cellulose hydrolysis were carried out using a stainless vessel batch reactor in an autoclave [10]. The pre-treated cellulose, SAC catalysts, and distilled water were mixed with a ratio of 10:1:4 (w/w/v) and placed in the reactor. Then, the reactor was placed in the autoclave and heated at a temperature of 130 – 140 °C for 4 hours. The mixture was cooled and filtered to obtain the liquid product. The obtained liquid product was tested qualitatively by using Fehling's reagent to identify the presence of reducing sugars.

3. Results and Discussion

3.1. X-ray diffractograms (XRD) analysis

The diffractogram patterns of the AC, SAC 60, SAC 80, and SAC 98 catalysts were shown in Figure 1. Overall, the diffractogram catalysts have similar patterns with two broad peaks in the range of 20°- 30° and 40°- 50°. These peaks indicate that the AC, SAC 60, SAC 80 and SAC 98 catalysts were amorphous. A broad peak at 20°–30° was associated with C (002) of the amorphous carbon structure containing randomly oriented aromatic carbon sheets. Whereas, peaks with lower intensity and broad at 40°–50° corresponded to C (101) in the graphite structure. These facts describe the crystallinity of carbon catalysts cannot be changed by the sulfonation process. However, the sulfonation process weakens the carbon sheet as the bonds break and increases the structural irregularity of the carbon [6].

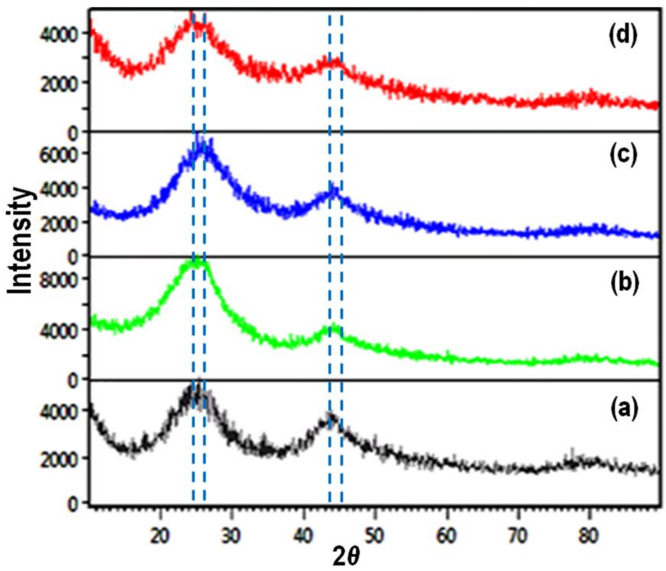

Fig. 1. The XRD patterns of (a) AC, (b) SAC 60, (c) SAC 80, and (d) SAC 98.

3.2. SEM Images analysis

The SEM images of non-sulfonated activated carbon and the sulfonated activated carbon catalysts were shown in Fig. 2. As shown in Fig. 2a, the morphology of AC surface was clearer and smoother compared to SAC 60 (Fig. 2b), SAC 80 (Fig. 2c) and SAC 98 (Fig. 2d). Increment of acid concentration during the sulfonation process was increased the damage percentage of the catalyst surface. In addition, the sulfonation process leads to the porous structure being rough and covered by $–SO_3H$ groups.

SEM image of AC shows clear, demonstrating in detail the surface morphology of these materials. The micrographs appearing in Fig. 2a and c exhibit an irregular and heterogeneous surface morphology with a well-developed and accented porous structure characteristic of carbonized organic waste [14]. The SEM micrographs of the sulfonated carbon catalyst surface morphology, shown in Fig. 4b and d, indicate a porosity decrease. This fact can be attributed to small defects, partial oxidation, condensation, and partial destruction of the porous structure arising from the strong sulfonating agent after the carbon functionalization process [13],[15]. It can also be inferred from the micrograph analysis that the partial pore blockage occurs due to the adsorption of $–SO_3H$ groups on the carbon support catalyst, confirming the efficiency of the sulfonation process [8].

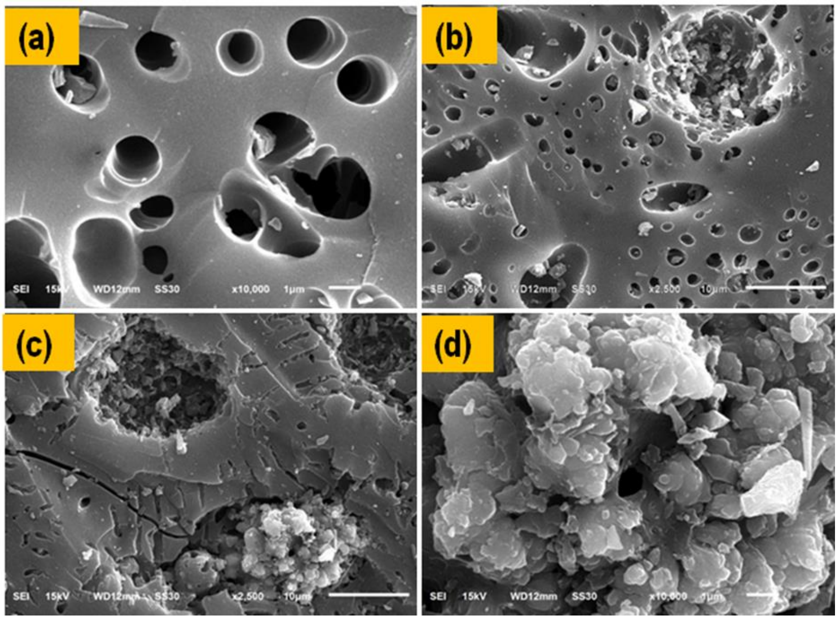

Fig. 2. The SEM image of (a) AC, (b) SAC 60 (c) SAC 80, and (d) SAC 98

3.3. FTIR spectrum analysis

The absence and existence of a sulfonate ($–SO_3H$) group attached to the activated carbon were identified by FTIR as shown in Fig. 3. The spectrum of AC was not shown the presence of the $–SO_3H$ group because there were no peaks at 3400 cm^{-1} and 1111 cm^{-1} (see Fig. 3a). Whereas, the spectra of SAC 60 (Fig. 3b), SAC 80 (Fig. 3b) and SAC 98 (Fig. 3c) show the presence of peaks in the range of 3448.52 – 3425.58 cm^{-1} and 1179.67 – 1111 cm^{-1}. These peaks represent the SAC catalyst's characteristic absorption of –SO3H groups. Table 1 shows the acidity of SAC catalysts were higher than that of AC catalyst. The acidity of the catalyst tends to increase with the concentration of sulfuric acid as a sulfonation precursor, which means that more sulfonate groups are bound to the activated carbon surface. It is well known the impregnated sulfonate group increases the acidity of the activated carbon catalysts. The high acidity of SAC catalysts can accelerate the hydrolysis of cellulose into glucose or simple sugar.

Table 1. The acidity of non- and sulfonated activated carbon catalysts

Catalysts	Acidity (mmol NH_3/g catalyst)
AC	0.0064
SAC 60	0.0146
SAC 80	0.0217
SAC 98	0.0255

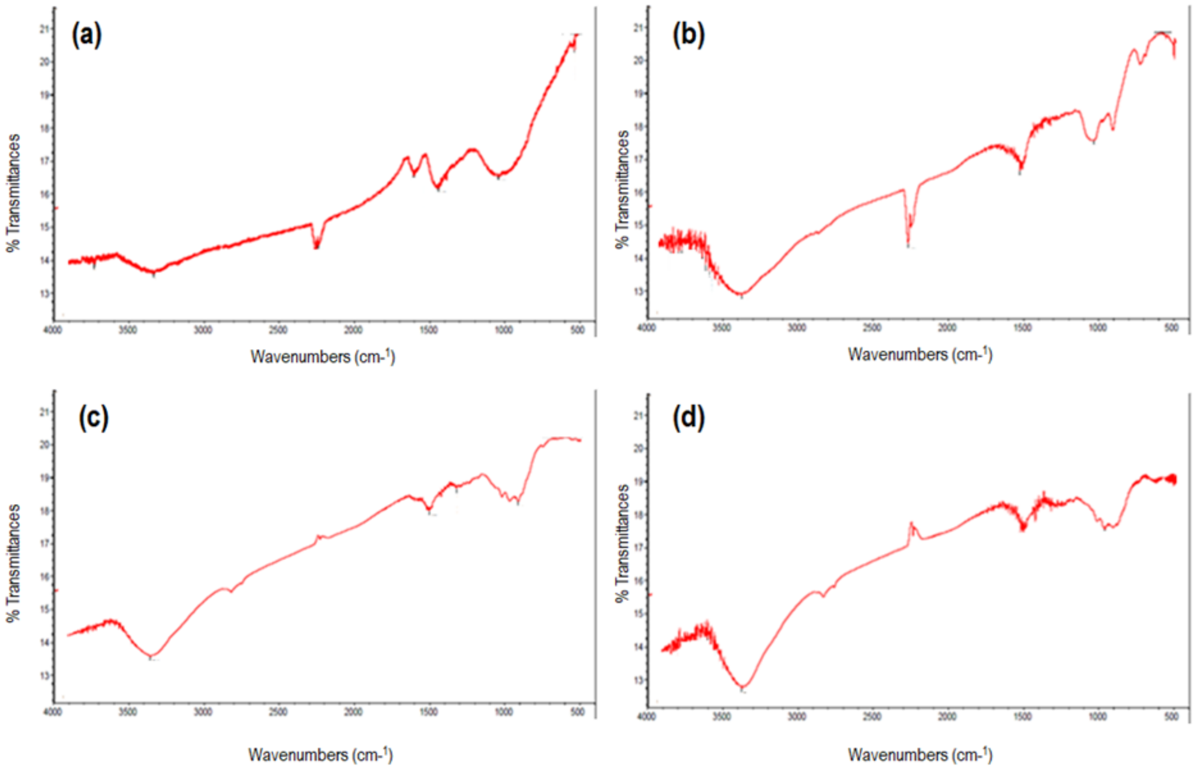

Fig. 3. Figure 3. FTIR spectra of catalysts: (a) AC, (b) SAC 60, (c) SAC 80, and (d) SAC 98.

3.4. Catalytic test

As described above, the hydrolysis process of the palm bunches cellulose bunches had been previously delignated with 10 % KOH solution and then followed by destruction with ionic liquid of BMIMCl. The SEM images of palm bunches of cellulose before and after pre-treatment with ionic liquid of BMIMCl were shown in Fig.4. The BMIMCl interacted with the lamellar structure of cellulose and the weak internal chemical bond of cellulose. Due to the palm bunch, cellulose fiber is not completely soluble in BMIMCl, consequently, the cellulose depolymerization and hydrolysis reactions are inhibited, and only a small part of the cellulose is broken down.

In preliminary experimental limits, the SAC catalysts can help hydrolyze palm fruit bunch cellulose into reduced sugars. As seen in Fig. 5, Fehling's reagent tests show positive results on the liquid product of hydrolysis of palm bunch cellulose. A brownish-red precipitate at the bottom of the test tube indicated the presence of simple reduced sugars (simple sugar) qualitatively. However, it is well known that Fehling's reagent tests are less precise enough to identify the type of simple sugar. Therefore, further analysis is needed to ensure the kind of reduced sugar in cellulose hydrolysis products.

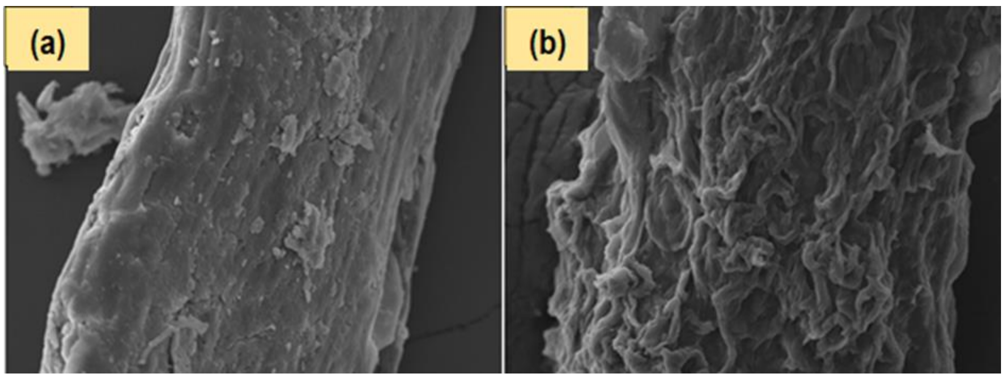

Fig. 4. The SEM images of palm bunch cellulose (a) before and (b) after treatment in BMIMCl.

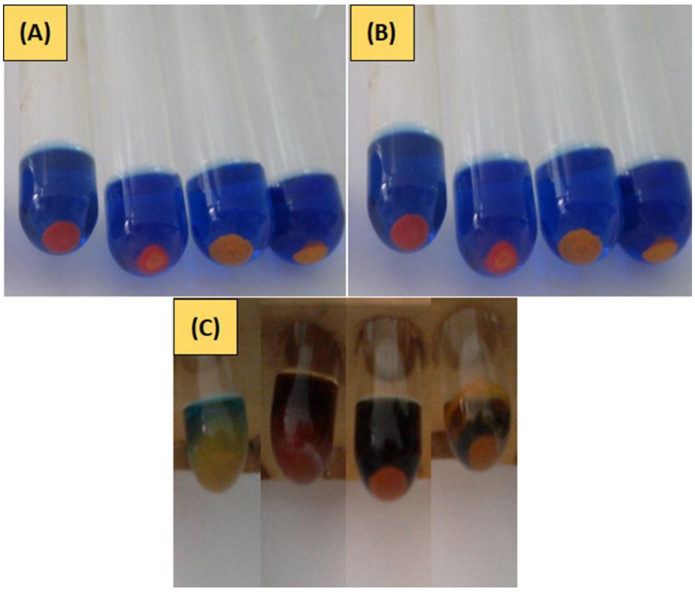

Fig. 5. Fehling tests of the liquid product of hydrolysis of palm bunch cellulose by using activated carbon-based catalysts: (a) SAC 60, (b) SAC 80, and (c) SAC 98

4. Conclusion

This work successfully synthesized the activated carbon-based catalysts such as AC, SAC 60, SAC 80, and SAC 98 from palm kernel shells. Based on the XRD analysis, the crystallinity of AC and SAC catalysts were amorphous. The presence of –SO3H groups on the surface of activated carbon-based catalyst has no positive effect on the crystallinity form. The SEM characterization shows the morphology of the AC surface was quite clear and smooth than the SAC catalyst. This means the sulfonation process affects the structure and pores on the surface. The green SAC catalysts may be a potential catalyst for the hydrolysis of palm bunch cellulose to simple sugar.

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