



Preparation and Characterization of Sulfonated Carbon from Candlenut Shell as Catalyst for Hydrolysis of Cogon Grass Cellulose into Glucose

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Cogon grass (*Imperata cylindrica*) is convertible into glucose by hydrolysis process, which usually requires a catalyst. A solid acid catalyst of sulfonated carbon was used in this work. This study aimed to observe the viability of candlenut shell as carbonaceous source in solid acid catalyst production and to characterize the sulfonated carbon. The carbonization was performed at 250-550 °C for 4 h, while sulfonation was carried out at 100-180 °C for 6 h. Sulfonated carbon was then characterized by H⁺ activity/acid density test, scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX) and Fourier transform infrared (FTIR) spectroscopy. Sulfonated carbon was then tested as a heterogeneous catalyst for hydrolysis reaction. The reaction was performed in a stainless steel batch reactor at 100 °C for 6 h. Glucose formed by hydrolysis was measured by dinitrosalicylic acid (DNS) method. Results of this study suggested that sulfonated carbon derived from candlenut shell may be used as a catalyst for cogon grass cellulose hydrolysis to produce glucose.

Keywords: Candlenut shell, Carbonization, Sulfonation, Cellulose hydrolysis.

INTRODUCTION

Cogon grass (*Imperata cylindrica*) is a potential renewable energy source because it is widely available, adapts readily to environment, grows quickly, and does not compete with food crops. In Indonesia, almost 10 million hectares of cogon grass is available. The cellulose of this cogon grass, which could reach 42.5% is convertible into glucose and in turn, be used as an alternate energy substrate or precursor of various industrial chemicals such as ethanol, organic acids, hydrocarbons and monomers [1]. Conversion of biomass based cellulose into glucose is attained through hydrolysis. The process usually requires inorganic acids or enzymes as catalyst. However, using inorganic acid is impractical as it causes equipment corrosion, complex product separation and environmental damage. On the other side, enzymes are still expensive and thus, uneconomical. To explore these issues, a solid acid catalyst of sulfonated carbon was proposed [2].

For solid acid catalyst production, carbon material used as catalyst support should be in polyaromatic hydrocarbon form. Such structure is achievable by carbonating carbon source at

± 400 °C. The carbon is then reacted with sulfuric acid to form sulfonated carbon. The resulting sulfonate groups containing H⁺ will behave similar to acids [3,4] and are expected to be bound to the aromatic structure [5]. Solid acid catalyst has the advantage of being non-corrosive, easy to separate and reusable. Carbon was selected as catalyst support due to its recyclability, large surface area, high catalytic activity and resistance to acid, base, temperature, pressure and chemicals [6,7].

The use of carbon as a catalyst support in cellulose hydrolysis has been reported in some literature, but was limited to the carbon derived from pine chips [8], corn stover, switch grass, prairie cord grass [9], bagasse [10] and palm kernel shells [11]. So far, the use of activated carbon from candlenut shells has never been reported. Therefore, this study aimed to evaluate candlenut shells as carbon source in solid acid catalyst production and its application in the cellulose hydrolysis.

EXPERIMENTAL

Candlenut shells were obtained from Tuntungan Sumatera Utara, while cogon grass was obtained from Tembung, Sumatera

Utara, Indonesia. Sulfuric acid, barium chloride, dinitrosalicylic acid reagents, sodium hydroxide and potassium sodium tartrate tetrahydrate (Rochelle salt) were purchased from local suppliers.

Catalyst preparation: Sulfonated carbon was produced using procedures informed by Ormsby *et al.* [8] and Fraga *et al.* [11] with modifications. After cleaning and washing, candlenut shell was heated in an oven at 110 °C for 2 h, followed by carbonization in the furnace at 250, 300, 350, 450 and 550 °C for 4 h. The resulting carbon was milled, sieved to 50 meshes, and reheated in oven at 110 °C for 1 h. Subsequently, 5 g carbon was mixed with 50 mL H₂SO₄ 96% solution in a glass beaker and stirred for 15 min. Afterwards, carbon containing H₂SO₄ was placed in a ceramic container and heated in a muffle furnace for 6 h at 100, 120, 150 and 180 °C to yield the catalyst. The catalyst was then cooled and washed with hot deionized water (90 °C) until no sulfate was tracked using BaCl₂ solution. Finally, it was dried at 110 °C for 24 h. The catalyst was characterized for its acid density, functional groups and morphology by titration, FTIR and SEM-EDX, respectively.

Cogon grass preparation: Cogon grass preparation procedures was done according to Li *et al.* [9] method with modification. Cogon grass was, consecutively, separated from its roots, washed with water to neutrality, cut, dried in oven at 105 °C for 2 h, pulverized in ball mill, sieved to 50 meshes, and finally stored in a sealed container.

Cellulose hydrolysis: Cellulose hydrolysis was done according to Ormsby *et al.* [8] and Li *et al.* [9] methods with some modifications. As much as 2.5 g dry cogon grass powder was introduced into a stainless steel batch reactor and then mixed with 1 g sulfonated carbon and 50 mL water. The process was carried out at 100 °C for 6 h. After completion, the mixture was analyzed quantitatively for its glucose content by dinitrosalicylic acid [12].

RESULTS AND DISCUSSION

Cogon grass analysis: Cogon grass was analyzed for its cellulose and water contents. Based on the result, fresh cogon grass contains 39.50% cellulose and 74% water. The cellulose content is similar to that in other literature at ± 40% [1].

SEM-EDX analysis: SEM analysis was done to observe the surface morphology of fresh candlenut shell, unsulfonated carbon from candlenut shell and sulfonated carbon from candlenut shell. For these samples, carbonization was conducted at 350 °C for 4 h and sulfonation at 120 °C for 6 h. The SEM results are shown in Fig. 1. In Fig. 1a, fresh candlenut shell has uneven and non-porous surface. This result is similar to that reported by other researchers [13,14]. This result also suggests that fresh candlenut shell has low surface area and probably low adsorption capability.

In Fig. 1b, carbon from candlenut shell retains its uneven surface, but pores start to appear on its surface. During carbonization, candlenut shell that consisted cellulose, hemicellulose and lignin decomposed and produced gas products. Formation of pores in carbon was due to the discharge of gas products at high temperatures. This finding is also similar to reports by other researchers [14,15], which suggests that carbonization may increase surface area through pore formation. In Fig. 1c,

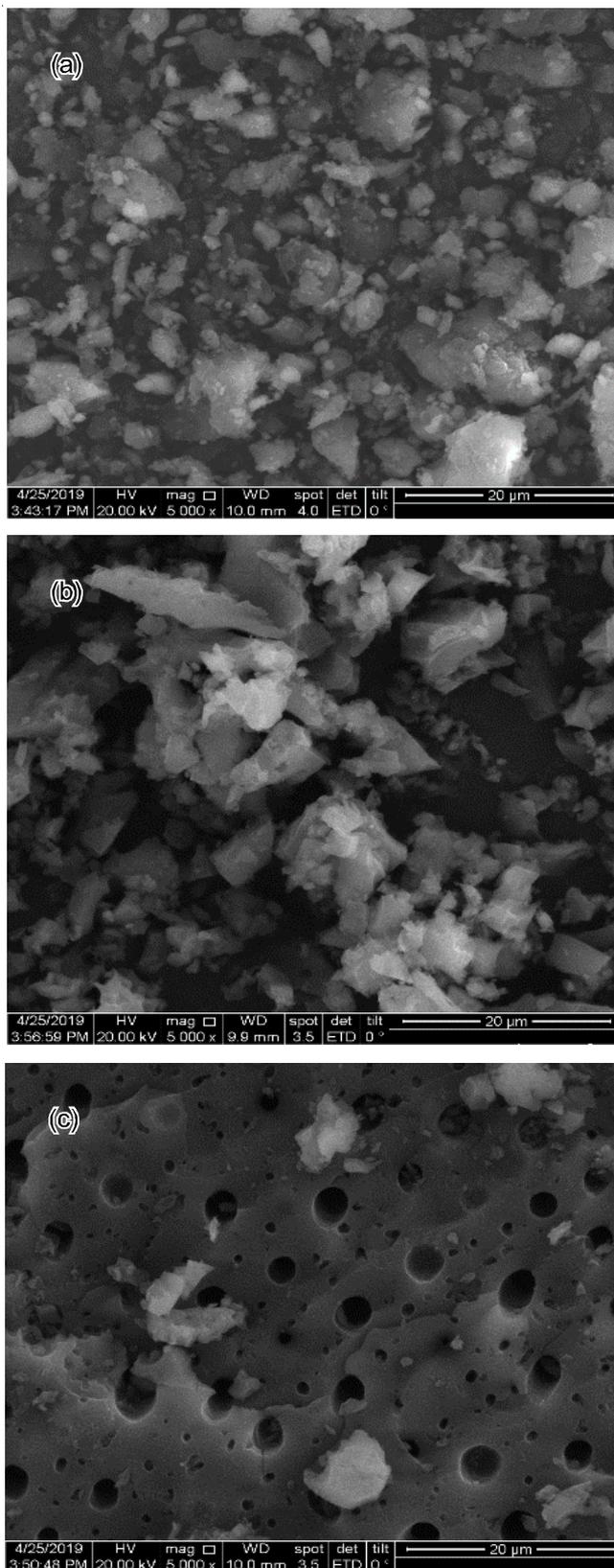


Fig. 1. SEM Analysis of (a) fresh candlenut shell, (b) carbon from candlenut shell, (c) sulfonated carbon

sulfonated carbon has more exposed but its surface has become flat. The number and size of pores also increased. This is important as pores act as reaction site, in which reactants diffuse into and are converted to products. Similar finding was reported

by Mardiah *et al.* [16] on sulfonated carbon from *Jatropha curcas*.

Results of EDX analysis on fresh candlenut shell, carbon from candlenut shell before sulfonation and carbon from candlenut shell after sulfonation are summarized in Table-1. In Table-1, carbon and oxygen are dominant in candlenut shell. After carbonization, carbon content increased while other elements such as oxygen and calcium declined. This is because during carbonization, carbon atoms will coalesce and form more stable bonds, while other compounds evaporate or detach [17]. After sulfonation, presence of sulfur was detected at 8.28%. This suggests that sulfonate groups has attached to carbon surface.

Element	Candlenut shell (%)	Un sulfonated carbon from candlenut shell (%)	Sulfonated carbon from candlenut shell (%)
C	42.57	78.64	62.33
O	46.19	17.87	26.28
Ca	9.73	3.49	3.11
Mg	1.51	–	–
S	–	–	8.28

FTIR analysis: The spectrum of candlenut shell carbon before and after sulfonation is presented in Fig. 2. From Fig. 2, both carbon samples had aromatic C=C at wavelength of 1508 cm^{-1} (before sulfonation) and 1557 cm^{-1} (after sulfonation), which is the characteristics of samples undergoing carbonization [8,11]. Phenol group or -OH carboxyl monomer group was also observed at wavelength of 3607 cm^{-1} (before sulfonation) and 3551 cm^{-1} (after sulfonation) [11,18]. This indicates that during carbonization, biomass decomposed and reformed phenolic compounds and polycyclic aromatic hydrocarbons. Several of the functional groups such as the aromatic ring will produce sulfonate groups on the catalyst surface after sulfonation. The sulfonate groups, which appear at wavelength of 1026 and 1197.79 cm^{-1} , was observed for the sulfonated carbon [8,11,19]. This suggests that sulfonation was successful. However, the presence of C=O carbonyl group at wavelength of about 1693.50 cm^{-1} suggests that sulfonation did not only form sulfonate groups but also other functional groups on the carbon surface [16,20].

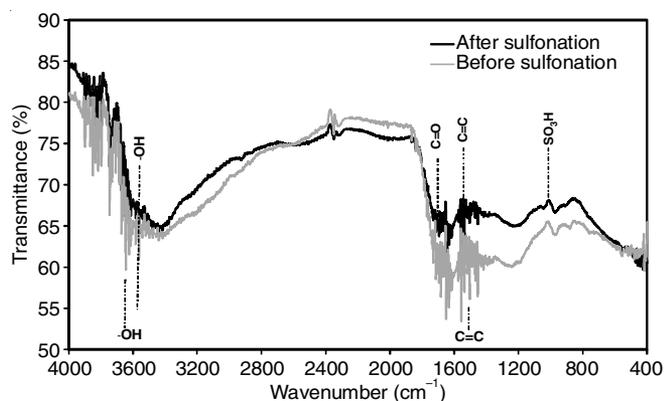


Fig. 2. FTIR of candlenut shell carbon before and after sulfonation

Acid density analysis: Fig. 3 depicts the effect of carbonization temperature on H^+ activity of sulfonate group (SO_3H) of the catalyst at various sulfonation temperature. The sulfonate group on the catalyst is regarded to be liable for the catalytic activity of the catalyst in cellulose hydrolysis. The sulfonated candlenut shell derived carbon catalyst was produced at a range of carbonization temperature ($250\text{--}550\text{ }^\circ\text{C}$) and sulfonation temperature ($100\text{--}180\text{ }^\circ\text{C}$).

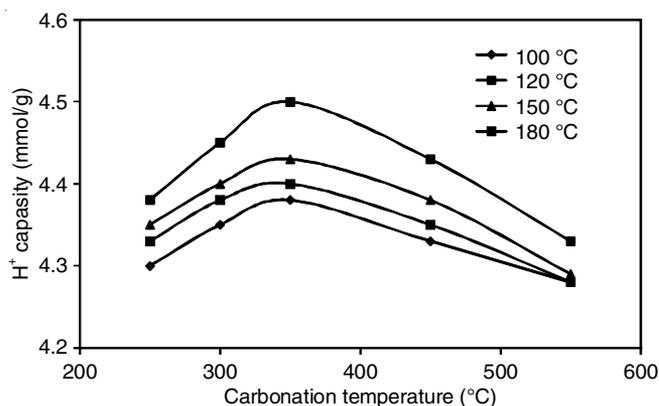


Fig. 3. Effect of carbonization temperature on H^+ activity of sulfonate group (SO_3H) of the catalyst at various sulfonation temperature

In Fig. 3, H^+ activity is highest at 4.5 mmol/g at carbonization temperature of $350\text{ }^\circ\text{C}$ and sulfonation temperature of $120\text{ }^\circ\text{C}$. The H^+ activity tended to increase with carbonization temperature up to $350\text{ }^\circ\text{C}$ and decreased afterwards, regardless of sulfonation temperature tested in this study. Higher carbonization temperature leads to better carbonization and induce the formation of more active aromatic carbons, which support sulfonation [21]. However, when carbonization temperature is too high, H^+ activity is negatively affected [21]. At high carbonization temperature, carbon structure is compressed further and the aromatic sheets enlarge and aligned tightly against each other, which restricts accessibility of sulfonate groups to the catalyst sites and hinders reactant diffusion [11,22]. At low temperature (less than $300\text{ }^\circ\text{C}$), carbon formation is not enough for application as catalyst support. Similar findings were also reported by other researchers [21,22]. Optimum carbonation temperature is reported to be within $300\text{--}400\text{ }^\circ\text{C}$ by many literatures, but the carbonaceous sources are different, namely oil palm shells [11] and bagasse [22]. Optimum carbonization temperature seems to depend on the carbonaceous source.

Also in Fig. 3, H^+ activity is affected by sulfonation temperature as well. Sulfonated carbon contains sulfonate groups which function as the active site of catalyst [3,4]. At fixed carbonization temperature, H^+ activity increased with sulfonation temperature up to $120\text{ }^\circ\text{C}$ then decreased afterwards. Similar finding was reported by Zhou *et al.* [21]. The H^+ activity reduction at sulfonation temperature beyond $120\text{ }^\circ\text{C}$ is possibly due to thermal damage on the carbon [21]. Similar phenomenon was also informed by Fraga *et al.* [11] using palm oil shells as the carbonaceous source.

Cellulose hydrolysis: In this study, sulfonated carbon with highest H^+ activity of 4.5 mmol/g was applied for cogon grass hydrolysis. Un sulfonated carbon and sulfuric acid were also used as comparison.

Glucose identification by FTIR: Glucose functional groups for hydrolysis catalyzed by sulfonated carbon and sulfuric acid were analyzed by FTIR. The result is presented in Fig. 4. In Fig. 4, there are vibrational spectra similarity between glucose from hydrolysis catalyzed by sulfonated carbon and sulfuric acid. Glucose spectra is specified usually as: the -OH vibrational stretching is computed to be in the area of 3876 to 3005 cm^{-1} , and the CH vibrations up to 2061 cm^{-1} . The strong C=O stretch from 1849 to 1634 cm^{-1} . A conjugation band of OCH and COH deformation occurs from 1526 to 1347 cm^{-1} . The in plane CH and OH transformation from 1362 to 1191 cm^{-1} can be found. A band of CO and C=C stretching is occurred from 1191 to 995 cm^{-1} [23].

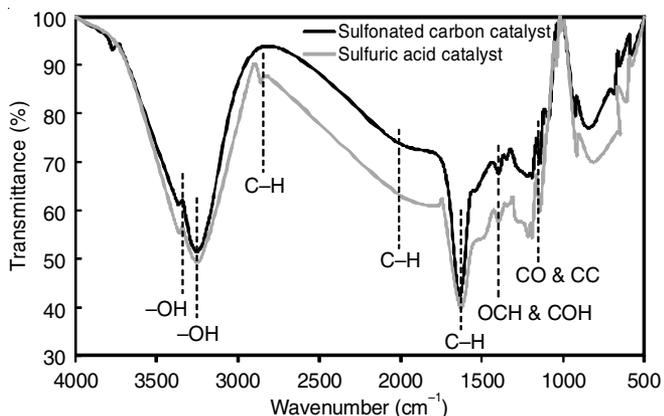


Fig. 4. FTIR analysis of glucose from hydrolysis catalyzed by sulfonated carbon and sulfuric acid

For glucose produced under sulfonated carbon catalyst, -OH vibrational stretching was observed at 3223, 3369 and 3772 cm^{-1} , while the CH vibrations were detected at 2023 and 2863 cm^{-1} . The strong C=O stretching was observed at 1639 cm^{-1} . For glucose produced under sulfuric acid catalyst, the -OH vibrational stretching was observed at 3365 and 3226 cm^{-1} . The CH vibration was observed at 2024 cm^{-1} . The C=O stretching was observed at 1632 cm^{-1} . For both samples, the conjugation band of -OCH and C-OH transformation was monitored at 1394 cm^{-1} , while the band of CO and C=C stretching was observed at 1138 cm^{-1} [23].

Analysis of glucose by UV-visible: Glucose concentration was determined by dinitrosalicylic acid using UV-Vis spectrophotometer. Comparison of glucose concentration obtained from hydrolysis using three types of catalysts is depicted in Fig. 5. In Fig. 5, glucose concentration of sample catalyzed by sulfonated carbon is higher than that catalyzed by unsulfonated carbon. This is due to sulfonated carbon having sulfonate groups which contain H^+ . The H^+ ions are responsible for the catalytic activity of sulfonated carbon during cellulose hydrolysis to break cellulose to glucose. Carbon after sulfonation contains sulfonate group as active site of carbon catalyst [3,4]. However, compared to sample catalyzed by H_2SO_4 , the glucose concentration of sample catalyzed by sulfonated carbon is still lower. This is due to sulfuric acid being a strong acid with higher acidity and the best acid for hydrolysis [9]. Comparison of acidity or H^+ activity of unsulfonated carbon, sulfonated carbon and 30% sulfuric acid is tabulated in Table-2.

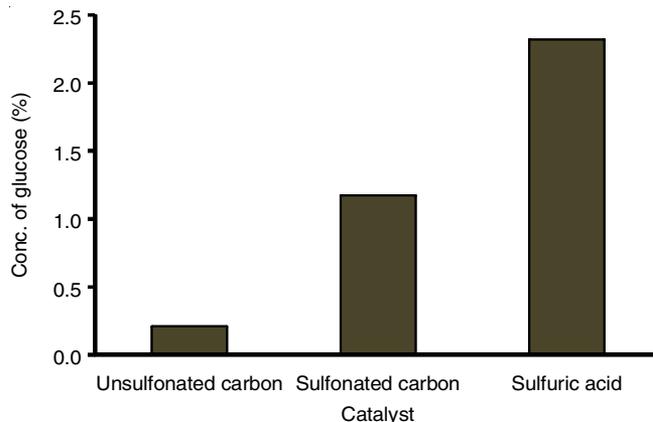


Fig. 5. Concentration of glucose obtained from hydrolysis using three types of catalysts: unsulfonated carbon, sulfonated carbon, and sulfuric acid

Catalyst	Acidity or H^+ activity of catalyst (mmol/g)
Unsulfonated carbon	0.10
Sulfonated carbon	4.50
Sulfuric acid (30% wt)	4.98

In this study, a glucose concentration of 0.21% and yield of 5.7% was obtained for sample hydrolyzed by unsulfonated carbon from candlenut shell. For sample hydrolyzed by sulfonated carbon from candlenut shell, glucose concentration was 1.17% and yield was 47% (higher than that obtained by Namchot *et al.* [10] at $\pm 33\%$). For sample hydrolyzed by H_2SO_4 , glucose concentration was 2.32% and yield was 96.3%.

Conclusion

A solid acid carbon catalyst from candlenut shell was successfully produced. Candlenut shell was carbonized to produce carbon and the carbon was reacted with conc. H_2SO_4 to produce sulfonated carbon. During sulfonation, number of pores increased and sulfonate groups were formed. The FTIR-spectra showed the peaks of $-\text{SO}_3\text{H}$ groups at wavelengths of 1026 and 1197.79 cm^{-1} produced from sulfonated carbon. The EDX results revealed that the sulfonated carbon contained 8.28% sulfur. These sulfonate groups catalyzed the cellulose hydrolysis. Based on H^+ activity, carbonization was optimum at 350 $^\circ\text{C}$ for 4 h and sulfonation was optimum at 120 $^\circ\text{C}$ for 4 h. Hydrolysis of 2.5 g cogon grass using 1 g solid acid carbon catalyst resulted in a glucose concentration of 1.17% and yield of 47%.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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