Green acidic catalyst from cellulose extracted from sugarcane bagasse through pretreatment by electron beam irradiation and subsequent sulfonation for sugar production

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Abstract

The objective of this research is to prepare a green acidic catalyst from cellulose derived from sugarcane bagasse (SB). Initially, SB was pretreated by electron beam irradiation with a dose of 50 kGy to 200 kGy and subsequent acid hydrolysis to obtain cellulose. The cellulose derived from SB was carbonized at different temperatures for 4 h and then sulfonated with heating at 120°C under reflux. Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) were used to confirm the successful preparation of acidic catalyst by irradiation pretreatment and subsequent sulfonation. The cellulose derived from irradiated SB at the lowest dose of 50 kGy was used as a representative irradiated sample for comparison with non-irradiation. Scanning electron microscope image of sulfonated biochar was observed pores with various sizes. The existence of sulfur atom onto sulfonated biochar surface was investigated by Energy dispersive X-ray spectroscopy. After sugar production by sulfonated biochar as an acidic catalyst, the total sugar content was measured by a phenol-sulfuric acid method using a UV-Vis spectrophotometer. The total sugar with $94.51 \pm 1.35\%$ content was found when the acidic catalyst was performed. It was remarkable to note that sulfonated biochar prepared from cellulose derived from SB after pretreatment and sulfonation exhibited outstanding result for being as an acidic catalyst for sugar production.

1. Introduction

Recently, Thailand was considered as the world's second-largest sugar production exporter, next to Brazil [1]. Numerous types of sugar product were exported such as sugarcane and sugar beets for feed and beverage industries. From the country background, Thailand was typically noted as an agricultural country. Thai people are working in the farm for various types of agricultural products such as rice, pineapple, palm oil as well as sugar.

Among various types of agricultural products, sugar was therefore considered as one of the most naturally bioresources in Thailand. It provided many health benefits including higher energy level, stronger immune system as well as better sleep. The use of sugar was therefore employed for all food industries and consequently caused sugarcane-based industries growth. However, with high amount of sugar production, bagasse was occurred in order of magnitude. The availability of bagasse was considered as an agricultural waste alongside sugar production factory. The existence of bagasse is useless and difficult to manage.

To the best of authors' knowledge, bagasse was structurally composed of cellulose. It was typically defined as a polysaccharide composed of a linear chain of β-1,4 linked D-glucose units. After sugar production, bagasse was typically defined as a solid waste. The presence of bagasse may result in extra-cost to manage. The use of bagasse for local farm was limited due to non-technical skill-worker. Therefore, to enhance the value of bagasse was extremely favorable. This concept was thus related to "Bio-Circular economy policy". No waste can be found in both municipal and industrial area.

To use bagasse with more efficiency, many researchers have extensively investigated. The use of bagasse can be employed as a reinforcement agent in order to form polymeric-based matrix composite. It provided an attractive application in numerous sectors such as food packaging, drug delivery system, medical technology as well as agriculture [2-4] . Recently, Azmin *et al.* [5] developed food packaging bioplastic film from cocoa pod husk cellulose incorporated with sugarcane bagasse fiber. The ratio of cellulose and fiber of 3:1 was optimal, based on water absorption percentage and water vapor permeability. Ben *et al.* [6] studied the synthesis of hydrogel from cellulose derived from sugarcane bagasse. Hydrogel exhibited excellent swelling characteristic. The swelling behavior of hydrogel generally increased after addition of polyvinyl alcohol into cellulose suspension. The use of cellulose significantly provided

many advantages due to high stiffness, high thermal stability as well as high water absorption.

Furthermore, one of the attractive applications was typically related to its fermentation ability. It can be converted to glucose and utilized as an alternative energy source. It can consequently be employed as a precursor for various chemical industries such as ethanol, organic acids as well as hydrocarbons by hydrolysis technique. This strategy was related to the conversion of cellulose from biomass to glucose by inorganic acids or enzymes as catalysts. Up to the present time, numerous acids such as H_2SO_4 [7], HF [8] and HCl [9] were employed for hydrolysis technique. It was utilized for conversion of cellulose to glucose for various levels of research involving academia and industrial commercialization. However, the use of inorganic acids was still limited in particular case such as complex product separation and environmental concern. Additionally, it offered the corrosion to research equipment. On the other hand, the use of enzymatic hydrolysis such as *Trichoderma viride* [10], *Trichoderma reesei* [11] and *Sporotrichum pulverulentum* [12] significantly provided the advantages including high level of extracellular cellulose for hydrolysis of cellulose. It was also limited due to cost. The process was difficult according to low efficiency of yield product. To preferably avoid the toxicity of acidic waste, acid catalysts in solid state was considerable to replace in order to be safe for environmental system.

Up to the present time, catalysts can be categorized into two distinct types. It was typically related to homogeneous catalysts [13]. The reactant and catalysts are in similar phase. Although the use of homogeneous catalysts provided high yield of product, it was limited due to the difficulty of separation after reaction. In contrast, the other one was noted as heterogeneous catalysts [14]. It was attractive due to easy separation, reusability as well as ability for scaling up for mass production. It was therefore resulted in economic benefit. Recently, several solid acid catalysts [15], including oxides [16], zeolites [17], cation exchanged resins [18], clays [19] and heteropoly acids [20] have been reported for the hydrolysis of cellulose. High concentration of fuming sulfuric acid was also employed. Hence, the use of catalysts derived from biomass provided numerous advantages including non-toxic and non-corrosive. It was also benefited due to low-cost of raw materials [21]. With the development of application and technology, electron beam was considered as a wonderful strategy for pretreatment of sugarcane bagasse. The benefit was related to simple operation, short processing time, easy control, large capacity and no chemical reagents usage. By virtue of this reason, electron beam irradiation is proper for pretreatment of sugarcane bagasse in order to gain cellulose in large-scale production [22-25]. Recently, furthermore, Sarosi *et al.* [26] used electron beam irradiation technique for cellulose pretreatment. It facilitates viscosity control and oxidation level by using ozone. Nagai *et al.* [27] used electron beam irradiation technique for conservation treatment of cellulose triacetate. This technique is considered as one of the most effective strategies for crosslinking reaction for being as photographic and cinematographic film. Similar to previous work of Kim *et al.* [28], radiation technique can be employed to prepared an eco-friendly carboxymethyl cellulose and carbon foam.

In this research work, we would like to present the preparation of solid based acid catalysts from sugarcane bagasse. Electron beam

irradiation was employed in combination with hydrolysis for pretreatment to obtain cellulose. Afterwards, cellulose was carbonized in order to form biochar. Sulfonation was therefore conducted to adhere sulfur atom onto biochar surface. Structural properties were then examined by Fourier transform infrared spectroscopy and X-ray diffraction. Scanning electron microscope with energy dispersive analysis was employed to evaluate the morphology. Brunauer-Emmett-Teller technique was used to determine the surface properties. Preliminary investigation as an acidic catalyst for sugar production was reported.

2. Experimental

2.1 Materials

Sugarcane bagasse (SB) was supplied from a local sugar factory in Thailand. Sodium hydroxide (NaOH) and urea (CH_4N_2O) were purchased from Merck, Co., Ltd. (Germany). Sulfuric acid (H_2SO_4) with 96% of concentration was purchased from Merck, Co., Ltd. (Germany). D (+)-Glucose anhydrous was purchased from Kemaus, Co., Ltd. (Australia). Phenol was acquired from Sigma-Aldrich, Co., Ltd. (USA). Potassium sodium (+)-tartrate was purchased from KemAus, Co., Ltd. (Australia). 3,5-Dinitrosalicylic acid, 98% was purchased from Acros organics, Co., Ltd. (Australia). All of chemical reagents were used as receive without further purification.

2.2 Methodology

2.2.1 Preparation of acidic catalyst

SB was cleansed with water and afterward dried in air oven at 50°C to a constant weight. After that, it was cut into the small pieces and then ground with grinding machine. The sample was filtered using an aluminum sieve to control the particle size with 300 μm. Subsequently, the sample was pretreated with electron beam irradiation at different doses. 10 mL of 3%v/v of sulfuric acid was added into 1 g of SB. After that, the sample was put into the round bottom flask and consequently heated at 100°C for 30 min under magnetic stirring. Then, it was washed with DI water several times until neutral pH. To form biochar, the sample was heated in a muffle furnace at temperature of 250°C, 350°C and 450°C for 4 h. The heating rate of $10°C \cdot min^{-1}$ was employed. The experiments were repeated three times to ensure the statistical average. To evaluate the quantity of products prepared from carbonization of pretreated SB at various temperatures, the yield percent of product was calculated by the following equation:

$$Yield\ (\%) = \frac{W_i}{W_p} \times 100 \qquad (1)$$

where W_p and W_i represent the weight of product after carbonization and the initial weight of pretreated sugarcane bagasse before carbonization, respectively.

For the sulfonation reaction, 5 g of biochar was poured into 50 mL of sulfuric acid. The mixture was stirred for 15 min in order to ensure the homogeneity. Consequently, the sample was refluxed at 120°C for 6 hours to form an acidic catalyst. The sulfonations were performed in triplicate for each of the samples.

2.2.2 Preliminary investigation of green acidic catalyst for sugar production

To evaluate the sugar production of acidic catalyst, 2.5 g of SB was mixed with 1 g of acidic catalyst. Subsequently, 50 mL of water was poured into the mixture. The reaction was refluxed for 6 h. After that, it was filtered by a vacuum filtration through 23 μm membrane filters to remove the solid phase. The solution phase was quantitatively analyzed for total sugar by UV–vis spectrometer at maximum absorption wavelength (λ_{max}) of 484 nm. The sugar productions were repeated in triplicate for each of the samples.

2.3 Instruments and characterization

2.3.1 Irradiation

The E-beam accelerator from a Mevex Corporation Ltd., Canada with Model MB 20-16 was employed for irradiation. Irradiation was performed at the Irradiation Center Klong 5, Thailand Institute of Nuclear Technology (Public Organization), Thailand. The energy and current of the electron beam were set to be 3 MeV and 10 mA, respectively. The radiation dose was set to be 0, 50, 100, 150 and 200 kGy, respectively.

2.3.2 Fourier transform infrared (FTIR) spectroscopy

The chemical structures of sample were investigated by FTIR spectroscopy in attenuated total reflectance (ATR) mode. The spectra were obtained in the frequency range of 4000 cm^{-1} to 650 cm^{-1} with 16 scans at a resolution of 2 cm^{-1}.

2.3.3 X-ray diffraction (XRD)

X-ray diffraction patterns were collected by a Bruker AXS (Germany) with CuKα radiation as an X-ray source, operating at 50 kV and 100 mA. The diffraction intensities were recorded from 10º to 60º, with a scanning rate of 0.02 2θ/min. Before analysis, the samples were stored in a desiccator to prevent moisture absorption.

2.3.4 Scanning electron microscopy (SEM), Energy dispersive X-ray spectroscopy (EDX) and Field emission scanning electron microscopy (FE-SEM)

The morphology of the biochar after carbonization was taken by scanning electron microscope (JSM-7800F SEM instrument (JEOL)). The accelerating voltage of 15 kV and a magnification of 5000x were employed. Before analysis, the sample was dried by an air oven and covered with gold under vacuum by using a sputter coater. Field emission scanning electron microscope (SU5000 (Hitachi)) was also performed. The accelerating voltage of 10 kV and magnification of 2000x were used to observe. Elemental analysis was conducted using an EDX spectrometer (INCA-350, Oxford) at an accelerating voltage of 15 kV.

2.3.5 UV–vis spectrometer

A UV–vis spectrometer (Evolution 300, UK) was employed to measure the total sugar after reaction by phenol-sulfuric acid method. The measurement was detected as maximum absorption wavelength (λ_{max}) of 484 nm and scan speed of 240 nm·min^{-1}.

3. Results and discussion

3.1 Characterization of cellulose derived from SB after pretreatment by electron beam irradiation and subsequent acid hydrolysis

Figure 1(a) presents the FTIR spectra of cellulose extracted from pretreated SB by irradiation and subsequent acid hydrolysis. The electron beam irradiation doses were set up to be 50, 100, 150 and 200 kGy. The sample without any irradiation step was also provided for comparison (Figure 1(a) (A)). It was remarkable to note that the role of electron beam irradiation with various doses did not significantly provide the change on chemical structural properties of cellulose. Both non-irradiated and all irradiated celluloses exhibited the similar features of FTIR spectra (Figure 1(a) (A-F). The peaks at 3338 cm^{-1}
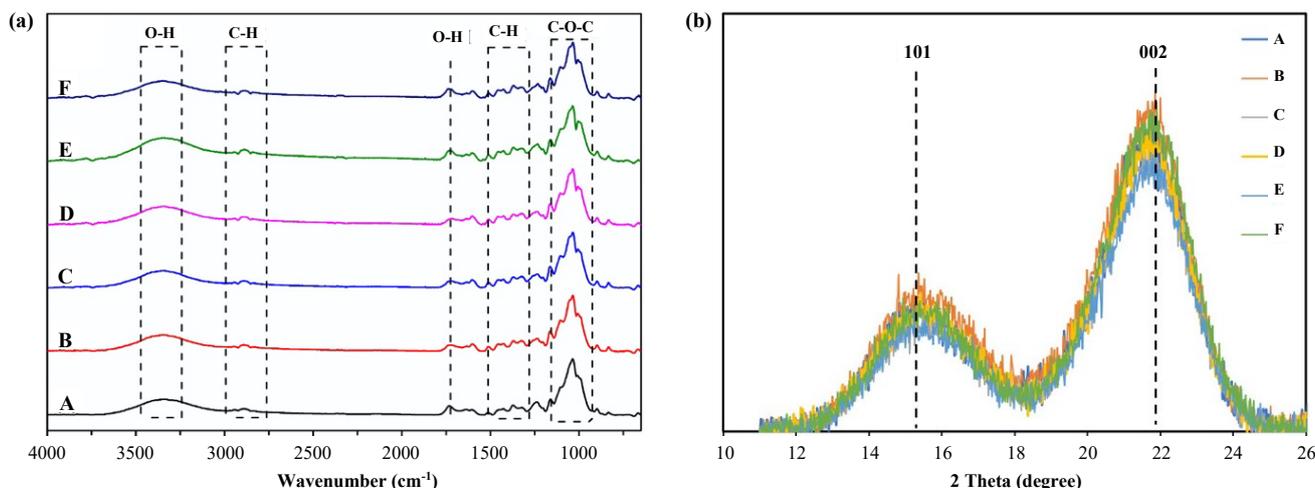

Figure 1. (a) FTIR spectra and (b) XRD patterns of cellulose derived from non-irradiated SB (A) before and (B) after hydrolysis; and cellulose derived from irradiated SB with electron beam irradiation at the doses of (C) 50 kGy, (D) 100 kGy, (E) 150 kGy and (F) 200 kGy after hydrolysis.

and 1733 cm^{-1} was observed, it was typically related to OH groups in cellulose structure [29]. The characteristic peaks at 2970 cm^{-1} and 1321 cm^{-1} to 1465 cm^{-1} were normally corresponded to the C-H stretching of cellulose structure. Strong characteristic peak at 1035 cm^{-1} was found due to the presence of C-O-C stretching. This was typically related to vibration of amorphous phase in cellulose.

To investigate the crystallinity of cellulose extracted from pretreated SB, XRD was employed. Figure 1(b) (B-F) displays the XRD patterns of cellulose derived from SB after irradiation (50 kGy to 200 kGy) and subsequent hydrolysis. The non-irradiated sample was provided for comparison (Figure 1(b) (A)). The similar XRD patterns were observed in all samples. According to FTIR results, the structural properties were insignificantly changed by electron beam irradiation and sulfuric acid hydrolysis. The characteristic peaks were existed at 15.3º and 22º. These peaks were corresponded to the diffraction plane [hkl] of (101) and (002) [30], respectively.

3.2 Preparation of biochar from cellulose derived from pretreated SB

To prepare biochar from cellulose derived from SB after irradiation and acid hydrolysis, only 50 kGy dose of electron beam irradiation was used as a representative. This is due to no change in chemical structure and crystallinity of cellulose at different doses. However, irradiation may improve the surface area and reactivity of SB. Hence, cellulose derived from irradiated SB at lowest dose of 50 kGy and subsequent hydrolyzed was used for further investigation. Biochar was prepared by carbonization technique at the temperatures of 250℃, 350℃ and 450℃. It was important to note that at the temperature of 250℃, it was insufficient temperature to transform from cellulose to biochar. The sample was still presented as a mixture phase of cellulose and biochar. With the presence of cellulose, ability to form acidic catalyst may not be completely occurred. Meanwhile, the increment of temperature up to 350℃ and 450℃, only biochar phase was observed. In order to investigate the structural properties of biochar prepared from carbonization of cellulose derived from pretreated SB, FTIR and XRD were performed. Figure 2(a) illustrates the FTIR

spectra of biochar prepared from cellulose derived from pretreated SB. In the case of carbonization temperature at 250℃ (Figure 2(a) (B)), the FTIR spectrum is similar to the pretreated SB before carbonization (Figure 2(a) (A)). This implied the incomplete transformation from cellulose to biochar. Nevertheless, the characteristic peak of C=C stretching at 1612 cm^{-1} was found, indicating in the formation of graphitic structure in the biochar. Moreover, the stretching vibration of hydroxyl group at 1733 cm^{-1} became weaker when compared with the pretreated SB before carbonization and then disappeared from biochar with increase of temperature (Figure 2(a) (C-D)). This is due to the loss of moisture and water in biochar at high temperature. For the FTIR spectra of biochar after carbonization temperatures at 350℃ and 450℃ (Figure 2(a) (C-D)), the two characteristic bands of aromatic C-H out-of-plane bending vibrations at 881 cm^{-1} and 790 cm^{-1} were observed [31]. Additionally, the strong characteristic peaks at 1612 cm^{-1} and 1406 cm^{-1} were also found, belonging to C=C stretching in polyaromatic ring [32]. These indicated that the cellulose was completely carbonized at high temperature, resulting in the appearance of aromatic rings. Besides, the functional C=O group at 1716 cm^{-1} was appeared in biochar after complete carbonization. This implied the enhancement of oxygen group content and improvement of reactivity in biochar surface.

X-ray diffraction technique was used to explore the crystallinity of cellulose and biochar obtained from carbonization of pretreated SB at different carbonization temperatures. For XRD pattern of cellulose extracted from pretreated SB (Figure 2(b)(A)), it exhibited the diffraction peak at 15º and 22º. The peaks were indexed to diffraction plane [hkl] of [101] and [002], respectively. It belonged to the crystalline cellulose, as suggested by previous literature of Alcaraz *et al.* [33]. In the case of the biochar prepared from carbonization of pretreated SB at 250℃ (Figure 2(b) (B)), it displayed XRD region of 15º and 22º, belonging to cellulose structure. However, the amorphous carbon or biochar structure was observed at the broad (002) band and illegible (100) band. This result was in agreement with FTIR result reported in Figure 2(a). The mixture between cellulose and biochar was presented at 250℃ due to incomplete transformation. By comparing XRD patterns of the biochar derived from carbonization of pretreated SB at 350℃
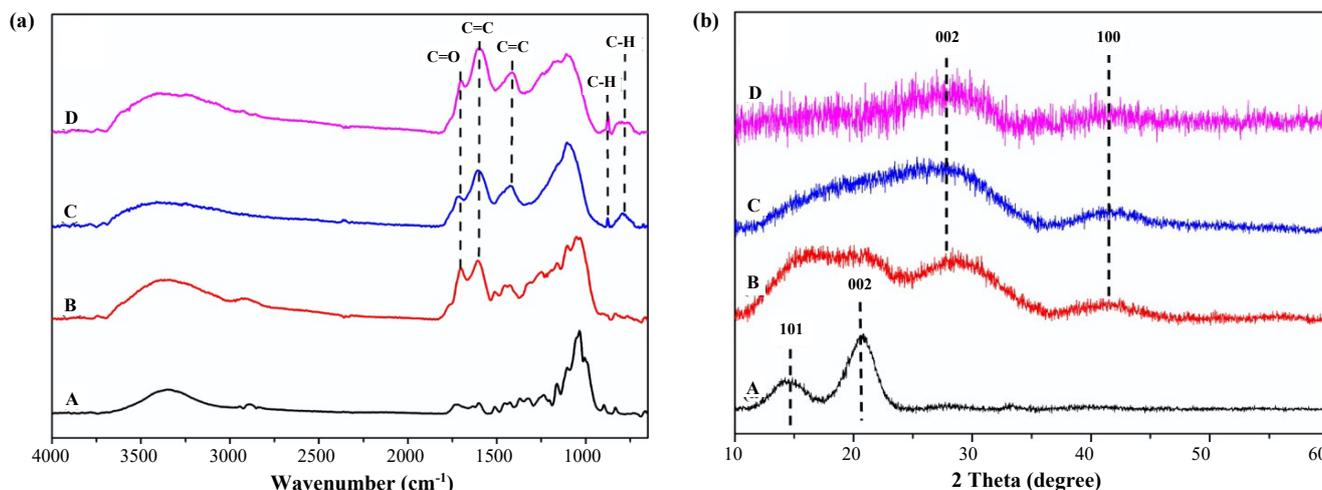

Figure 2. (a) FTIR spectra and (b) XRD patterns of (A) cellulose derived from pretreatment of SB by irradiation at 50 kGy and subsequent hydrolysis; and biochar obtained from carbonization of pretreated SB at the temperatures of (B) 250℃, (C) 350℃ and (D) 450℃.

and 450°C (Figure 2(b) (C-D) with 250°C (Figure 2(b) (B)), they were found the low intensity of diffraction band at 28º and 41º without the crystalline cellulose phase at 15º and 22º. This is in agreement with previous work of Xia *et al.* [34]. The layer spacing and domain size of crystallinity in cellulose structure decreased due to the carbonization with high temperature.

The yield percent of product derived from carbonization of pretreated SB (irradiation at 50 kGy and hydrolysis) was plotted as a function of the carbonization temperature, as shown in Figure 3. The yield percent of product were presented as $64.09 \pm 0.23\%$, $29.24 \pm 0.56\%$ and $18.78 \pm 1.12\%$ for carbonization temperatures of 250°C, 350°C and 450°C, respectively. It was decreased in contrast to increment of carbonization temperature. This can be explained that at high temperature, the long chain of cellulose fragments was gradually cracked into short fragments, resulting in the reduction of percent yields. Based on the results, it pointed out that the use of temperature at 350°C is sufficient for preparation of carbon-based material derived from biomass owing to the high yield and purity of biochar.

Figure 4 reveals the morphological properties of biochar prepared from carbonization of pretreated SB at the temperatures of 250°C, 350°C and 450°C. All of microstructural images were observed in the similar feature. The morphology showed smoothness of surface. This was indicative that electron beam technique and subsequent sulfuric acid hydrolysis for pretreatment can remove the impurities from biomass, as suggested by Zhang *et al.* [35]. After pretreatment or de-lignification, lignin was removed but cellulose exhibited no crack in among fibril bundles.

3.3 Sulfonation of biochar derived from cellulose extracted from pretreated SB

To modify biochar derived from cellulose extracted from pretreated SB as an acidic catalyst for sugar production, sulfonation reaction was employed to functionalize for the presence of sulfur atom onto carbon surface. The sulfonic acid group was formed by sulfonating agent onto biochar structure. Figure 5(a) exhibits the FTIR spectrum of sulfonated biochar (Figure 5(a) (B)) in comparing with unsulfonated biochar (Figure 5(a) (A)). After sulfonation (Figure 5(a) (B)), the characteristic peak at 1039 cm^{-1} was obviously seen, providing the presence of –SO$_2$– symmetric stretching in sulfonate group (–SO$_3$H) [36]. The successful sulfonation reaction onto biochar surface was therefore confirmed. The C=O stretching in COOH group at 1716 cm^{-1}

was slightly increased [37]. Moreover, the presence of C=C stretching (at 1615 cm^{-1} and 1406 cm^{-1}) and C-H bending vibration (at 881 cm^{-1} and 790 cm^{-1}) were still existed in the FTIR spectrum of sulfonated biochar (Figure 5(a) (B)). This indicated that the aromatic structure of biochar was also included in sulfonated biochar after sulfonation.

Figure 5(b) shows the XRD patterns of biochar before and after sulfonation. The diffraction angles were presented as two broad peaks at 25º and 43º. These peaks were indexed with diffraction plane of (002) and (100), respectively. The occurrence of both peaks was indicative that the material involved the aromatic structure oriented in a turbostratic structure, a mixture of sp^2 and sp^3 hybridized carbon, suggested by *Zeng et al.* [38]. In XRD pattern of sulfonated biochar (Figure 5(b)), the XRD diffraction peak was slightly displaced. This pointed out the rearrangement in lattice of polyhexagonal carbon atoms, cited by B*edin et al.* [39]. The FTIR and XRD results confirm the presence of –SO$_3$H groups on a biochar as an acidic catalyst.

To study the quantitative change of sulfonate group onto biochar, FTIR intensity ratios of I$_{1039}$/I$_{1615}$ and I$_{1039}$/I$_{1406}$ were determined; where I$_{1039}$ is the FTIR intensity of –SO$_2$– stretching vibration in sulfonate group of sulfonated biochar, I$_{1406}$ and I$_{1615}$ are the FTIR intensities of C=C stretching in aromatic ring of biochar. Since there is no sulfonate group in biochar before sulfonation, the appearance of the –SO$_2$– peak in sulfonated biochar proved the successful sulfonation. I$_{1406}$ and I$_{1615}$ were used as references to calculate the amount of sulfonate group onto sulfonated biochar.
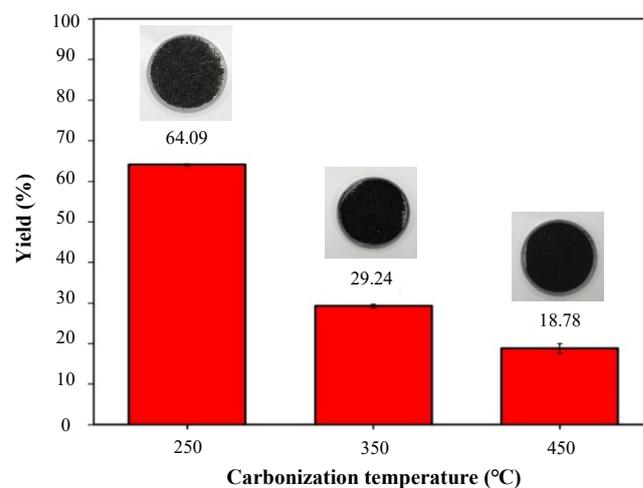

Figure 3. Yield percentage of product obtained from carbonization of pretreated SB at different temperatures.
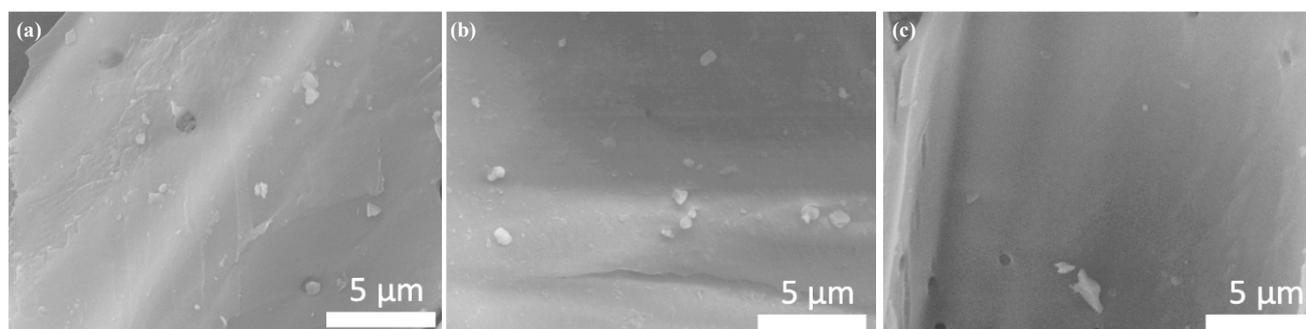

Figure 4. SEM micrographs at 5000x magnification of biochar prepared from carbonization at temperatures of (a) 250°C (b) 350°C and (c) 450°C of cellulose extracted from pretreated SB.
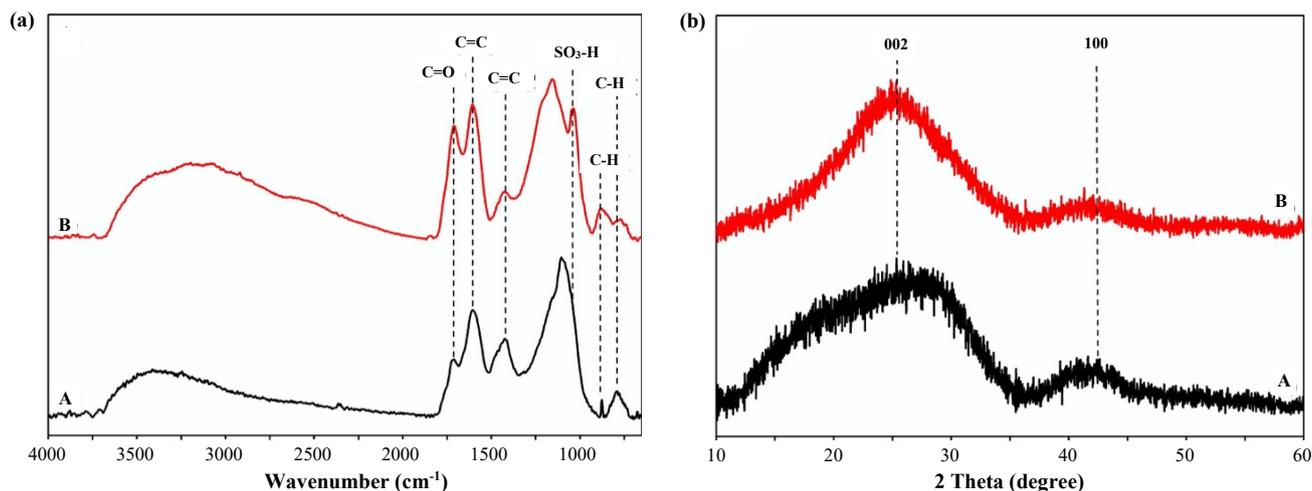
Figure 5. (a) FTIR spectra and (b) XRD patterns of biochar prepared from carbonization at 350℃ of cellulose derived from pretreated SB; (A) before and (B) after sulfonation.

Table 1. Intensity ratios (I_{1039}/I_{1615} and I_{1039}/I_{1406}) of different samples.

Samples	Intensity ratios	
	I_{1039}/I_{1615}	I_{1039}/I_{1406}
Unsulfonated biochar prepared from carbonization at 350℃ of non-pretreated SB	-	-
Sulfonated biochar prepared from carbonization at 350℃ of cellulose extracted from pretreated SB with only hydrolysis	0.435 ± 0.031	0.925 ± 0.022
Sulfonated biochar prepared from carbonization at 350℃ of cellulose extracted from pretreated SB with both irradiation at 50 kGy and hydrolysis	1.031 ± 0.072	2.680 ± 0.037

From Table 1, the FTIR intensity ratio of I_{1039}/I_{1615} in sulfonated biochar obtained from carbonization of pretreated SB with only hydrolysis process was 0.435 ± 0.031. Meanwhile, the FTIR intensity ratio (I_{1039}/I_{1615}) of biochar prepared from carbonization of pretreated SB with irradiation at 50 kGy and subsequent hydrolysis was 1.031 ± 0.072. This phenomenon was correspondingly observed in I_{1039}/I_{1406} ratio. It is noteworthy that irradiation at 50 kGy in pretreatment process enhanced the modification of sulfonate group onto biochar. This may be a result of the greater surface area of SB after irradiation.

SEM was used to explore the microstructural properties of biochar before and after sulfonation. As Figure 6(a), it can be seen the smooth surface of the biochar obtained from carbonization of original SB. The change on morphology was observed when it was sulfonated as displayed in Figure 6(b). After sulfonation, the biochar reveals the roughness of surface. This is possibly due to the heating and adding of acid during sulfonation process. For sulfonated biochar prepared from carbonization at 350℃ of cellulose extracted from pretreated SB (Figure 7(c)), the morphology consisted of porous with diameter of 17.19 ± 4.13 μm. This implies the high capability of the active sites of –SO_3H groups onto substrate for sugar production.

To confirm the existence of sulfur atom onto modified biochar after sulfonation, energy dispersive analysis was used to investigate as Figure 6. The elemental composition of unsulfonated biochar prepared from carbonization at 350℃ of cellulose extracted from nonpretreated SB was composed of carbon (69.27 wt%) and oxygen (30.73 wt%). After sulfonation, the presence of sulfur atom was occurred on the surface of biochar. This implied that the -SO_3H functional group was functionalized onto biochar. It is important to note that pretreatment of SB by irradiation at 50 kGy and subsequent

hydrolysis prior to carbonization and sulfonation leads to the high amount of sulfur atom (4.02 wt%), comparing with biochar obtained from carbonization at 350℃ of cellulose extracted from pretreated SB with only hydrolysis process (0.33 wt%).
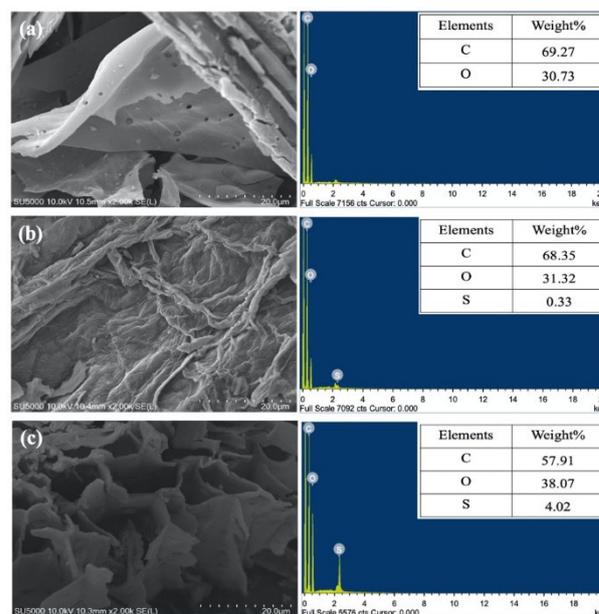

Figure 6. Morphological and elemental analysis of (a) unsulfonated biochar prepared from carbonization at 350℃ of cellulose extracted from non-pretreated SB, (b) sulfonated biochar prepared from carbonization at 350℃ of cellulose extracted from pretreated SB with only hydrolysis process and (c) sulfonated biochar prepared from carbonization at 350℃ of cellulose extracted from pretreated SB with both irradiation at 50 kGy and hydrolysis.

3.4 Preliminary investigation of green acidic catalyst for sugar production

Figure 7 displays the standard curve of total sugar analysis by the phenol-sulfuric acid procedure. The concentration of the standard solution was specified to be between 0.02 mg·mL^{-1} to 0.14 mg·mL^{-1}. It was found that the standard solution was presented as light orange to dark orange with respect from low to high concentration. After that, the standard solution is used to measure by UV–vis spectrometer at a wavelength of 400 nm to 600 nm, and the maximum absorption wavelength (λ_{max}) is discovered to be 484 nm. Obtaining a straight-line equation at y = 7.0336x – 0.1462 and R^2 = 0.9906. This process was studied by the method of Dubois *et al.* [40].

The total sugar content was measured in a phenol-sulfuric acid method using a UV-Vis spectrophotometer. In Figure 8, the total sugar concentration of sulfonated biochar catalysts is higher (73.26 ± 3.43% and 94.51 ± 1.35%) than that of unsulfonated biochar catalyst (51.18 ± 4.31%). This can be explained from the fact that sulfonated biochar catalyst had a sulfonate group as an active site which contained H$^+$ ion. Hence, the sulfonated biochar catalyst showed the greater catalytic activity to break cellulose for sugar production than unsulfonated biochar. Furthermore, considering in sulfonated biochar prepared from pretreated SB with both irradiation at 50 kGy and hydrolysis, it exhibited the excellent catalytic catalyst with the total sugar concentration of 94.51 ± 1.35%. This is due to the high amount of sulfonate group onto biochar as aforementioned. On the other hand, the total reducing sugar in other researches are approximately 40% to 70% [41,42]. The obtained results proved that sulfonated biochar prepared from pretreated SB with both irradiation at 50 kGy and hydrolysis processes can be used as a green acid catalyst which supported to bio circular economy policy for reused and value added the agro-waste.
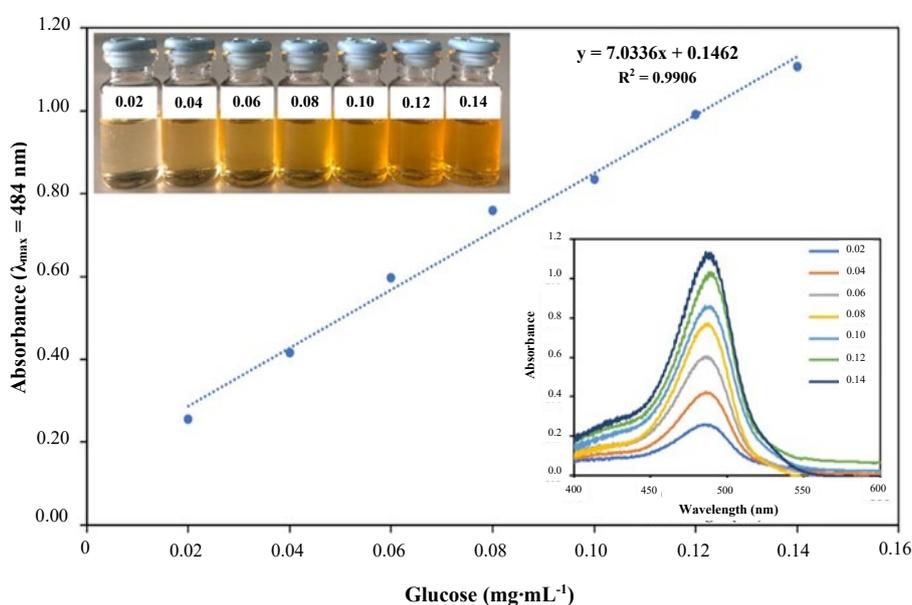

Figure 7. Standard curve of total sugar analysis by the phenol-sulfuric acid procedure.
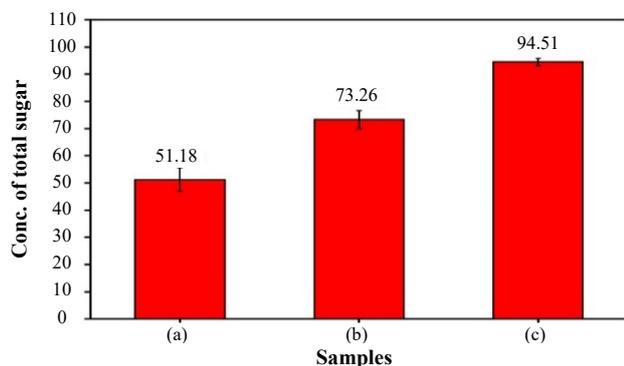

Figure 8. Concentration of total sugar achieved by using three different samples: (a) unsulfonated biochar prepared from carbonization at 350°C of cellulose extracted from non-pretreated SB, (b) sulfonated biochar prepared from carbonization at 350°C of cellulose extracted from pretreated SB with only hydrolysis process and (c) sulfonated biochar prepared from carbonization at 350°C of cellulose extracted from pretreated SB with both irradiation at 50 kGy and hydrolysis.

4. Conclusions

In this study, a green acidic catalyst from cellulose extracted from SB was successfully prepared. SB is pretreated with an electron beam irradiation dosage of 50 kGy. Then it was hydrolyzed to gain cellulose. Whenever cellulose was exposed to electron beam irradiation, no changes in its chemical structure were observed. It was then carbonized at 350°C for 4 h and sulfonated at 120°C for 6 h. The FTIR peak of SO$_3$H showed at a wavenumber of 1039 cm^{-1}. According to the EDX results, the sulfonated biochar prepared from carbonization at 350°C of cellulose extracted from pretreated SB with both irradiation at 50 kGy and hydrolysis contained 4.02% sulfur. The green acid catalysts prepared from carbonization at 350°C of cellulose extracted from pretreated SB can be hydrolyzed to quantify the total sugar. It was remarkable to note that SB was considered as one of the most important candidates for being as a raw material to develop as a solid acid catalyst for sugar production in near future.

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