

Research Article

Synthesis and Characterization of 5-Hydroxymethylfurfural from Corncob Using Solid Sulfonated Carbon Catalyst

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5-Hydroxymethylfurfural as a versatile organic compound is considered as a promising biomass-derived product via hydrolysis followed by dehydration of lignocellulosic biomass using solid catalysts. In this study, lignocellulosic materials (corn cob) were utilized to synthesize 5-hydroxymethylfurfural via solid acid catalytic conversion. The precursor of the catalyst material was chemically impregnated with $ZnCl_2$ prior to carbonization. The solid catalyst was prepared with three different acid concentrations of 98%, 96%, and 94% of sulfuric acid. The prepared catalyst was characterized by acid density elemental analysis, FTIR, XRD, and SEM. The maximum result of the total acid density and amount of SO_3H group was recorded as 3.5 mmol/g and 0.61 mmol/g, respectively, with high sulfur content of 1.87%. The result from FTIR spectra of $BC-SO_3H_{-1}$ confirms the incorporation of $-SO_3H$ groups into the carbon material. $BC-SO_3H_{-1}$ was selected based on the acid density and elemental analysis of the catalyst. The activity of the selected catalyst ($BC-SO_3H_{-1}$) was studied on the transformation of corn cob to 5-hydroxymethylfurfural using biphasic solvent (water: ethyl acetate) and NaCl in the reaction medium. The intermediate result in the hydrolysis/dehydration reaction was analyzed using FTIR and the functional groups observed confirm the occurrence of 5-HMF in the intermediate reaction result.

1. Introduction

The main source of functionalized carbon skeletons for the fine chemical industry, as well as for thermal and energy transportation, is still based on the fossil-fuel reservoir [1]. However, due to the depletion of world fossil fuel reserve, the increasing of its price and its negative environmental impact has pushed the world to look for alternative renewable fossil reserve and energy sources. Biofuels in comparison to fossil fuels should be relatively cheap and rich in energy, locally produced (saving foreign currency), have environmental benefits (low greenhouse gas emission), and be producible in large quantities without impacting on food supplies.

Transformation of biomass, which is abundant and inexpensive renewable resource into fuels, chemicals, and

materials precursors, has a great significance to decrease the excessive dependence on fossil resources, alleviate the energy crisis, reduce the environmental pollution, and promote the sustainable development of the whole human society [2].

Most researched sources of cellulose and hemicelluloses are bagasse, paper-pulp residue, bamboo, grain hulls, corncobs, wheat and rice straw, nutshells, rice husk, cottonseed, and wood (soft and hardwood). A corn cob is a major part of the corn's waste. It is estimated that 40–50% of corn is corn cob. It has been used as firewood or returned to the field. Corn cob contains 69.2% cellulose, 22.8% hemicellulose, and 8% lignin [3]. Cellulose and hemicellulose can be depolymerized into monosaccharide's like glucose, fructose, and xylose [1]. Cellulose, which is composed of β -1, 4-glycosidic bonds of D-glucose, has a highly ordered crystal structure owing to the hydrogen-

bond network between hydroxyl groups. As a result, it is difficult to degrade and is insoluble in conventional solvents, such as water [4].

Cellulose and hemicellulose can be hydrolyzed, which on further dehydration produce furan compounds (5-HMF and furfural) [5]. Among various desired compounds, 5-hydroxymethylfurfural (5-HMF) is considered as a versatile platform compound and a crucial intermediate for connecting biomass resource and fossil industry, and this is because it can be further transformed into a series of high-quality fuels such as ethyl levulinate (EL), 5-ethoxymethylfurfural (EMF), 2,5-dimethylfuran (DMF), C₉-C₁₅ alkane, and high-value chemicals such as levulinic acid (LA), 2,5-dihydroxymethylfuran (DHMF), 2,5-diformylfuran (DFF), and 2,5-furan dicarboxylic acid (FDCA) [2]. In addition, furfural derivatives have a wide industrial application like in oil refining, agrochemical industry, pharmaceuticals, and bioplastic (see [6]). The routes for converting cellulose into 5-HMF are illustrated in Scheme 1.

Among 5-HMF derivatives, 2,5-dimethylfuran (DMF) is particularly attractive. This is due to the high potential for mass production with high rate and higher energy content than the current market-leading bioethanol. DMF possesses a higher energy density (31.5 MJ·L⁻¹), similar to that of gasoline (35 MJ·L⁻¹) and 40% greater than that of ethanol (23 MJ·L⁻¹). In addition, higher octane number (119), lower volatility (bpt. 92–94°C), lower separation energy consumption, and immiscibility with water are observed [6]. Thus, DMF is more similar to gasoline than bioethanol as a new-generation biofuel. The hydrogenolysis of 5-HMF produces 2,5-dimethylfuran (DMF) and a potentially good gasoline component, with heating value (35 MJ/kg) and boiling point (93°C) higher than those of ethanol (22.6 MJ/kg and 78°C, respectively) [7].

Therefore, exploring alternatives to fossil fuels is of great importance. One of the most promising alternatives is biomass, owing to its abundance and renewable nature. 5-Hydroxymethylfurfural is one of the most promising biomass platforms. It holds a key position in the production of liquid biofuels and biomass-derived intermediates including a vast number of chemicals. In this project, the chemical compositions of corncob can be attributed as a raw material for synthesis of 5-hydroxymethylfurfural, which is a platform chemical that can be transformed to a variety of value-added chemicals and fuels. Producing chemical precursors like 5-hydroxymethylfurfural reduces or saves foreign currency due to importing and will provide a new step toward achieving renewable biomass-based chemicals and fuels platform.

In catalytic hydrolysis-dehydration of lignocellulose biomass, the action of catalyst is the limiting step in catalytic reaction process. Homogeneous catalysts such as HCl and H₂SO₄ have been used in hydrolysis of lignocellulose biomass. However, they suffer from problems of product separation, reactor corrosion, poor catalyst recyclability, and the need for treatment of waste effluent. On the other hand, the use of heterogeneous solid acids can solve some of these problems through the ease of product separation and good catalyst recyclability [8].

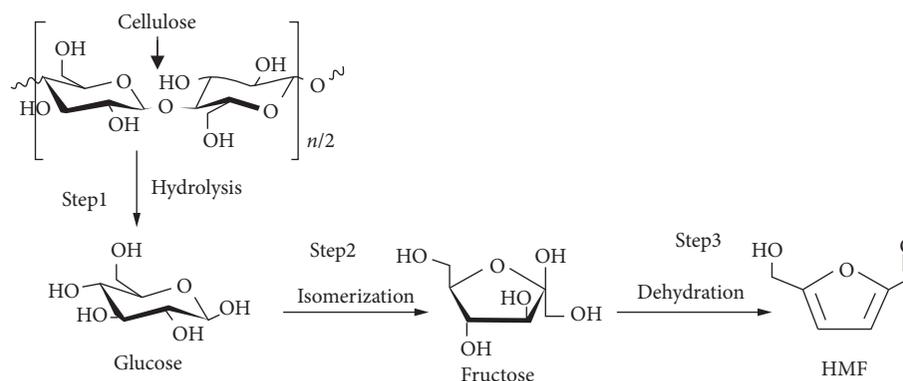
2. Materials and Methods

2.1. Raw Material Collection and Sample Preparation. Corncob was locally collected around Zenzelima farms, 15 km from Bahir Dar City, Ethiopia. The collected corncob was washed with water to remove dust and unwanted materials. It was dried in an oven at a temperature of 60°C for 48 hr. Then, the sample was reduced using hands and milled with milling machine and sieved to below 1 mm particle size. The sieved sample was kept in a closed container for use as a main raw material for the production of 5-hydroxymethylfurfural.

2.2. Collection and Preparation of Catalyst from Bamboo Wood. Bamboo wood (Bambusoideae), bought from furniture houses, was manually crushed and milled using milling machine. Then, the milled bamboo wood was sieved in order to obtain the desired size of bamboo wood powder (0.4–1.5 mm). The powder was then dried in an oven for 12 hours at 100°C to reduce its moisture content and stored in plastic bags for the next purpose.

2.2.1. Chemical Activation and Carbonization of Bamboo Wood Powder. Dried bamboo wood powder was chemically activated with zinc chloride, which can assist in lowering temperature and shortening time for activation and improving the development of inner porosity. 10–15 gm of bamboo powder was impregnated with 20 wt.% zinc chloride in a beaker containing 50 ml 1 M HCl solution, under mechanical agitation at 25°C for 15 hrs. The solid part was separated by filtration and oven-dried at 80°C for about 24 hrs. The dried impregnated bamboo powder was then pyrolyzed in a Nabertherm furnace at a specified temperature in an inert atmosphere. The pyrolysis process was undergone at a temperature of 450°C for 1 hr. Then, the obtained impregnate was discharged from the furnace and soaked first in warm (100°C) aqueous HCl solution (5%) for 1 hour followed by rinsing with warm distilled water (50°C) for several times to remove the ash content of activated carbon until the pH of the washed water was neutral. Then, it was dried at 80°C in an oven for approximately 24 hrs.

2.2.2. Functionalizing Chemically Activated Carbon via Sulfonation. Functionalization of the impregnated activated carbon via sulfonation was done according to the method reported by [9]. 10–15 gm impregnated activated carbon was then functionalized by heating for 12 hours in concentrated H₂SO₄, (100 ml) in round bottom flask at 180°C. The sulfonation was undergone at three different concentrations of H₂SO₄, (98%, 96%, and 94%). After heating, the slurry was placed in cold water and then filtered. Then the sulfonated solid catalyst was washed with warm distilled water until the wash water was neutral. Finally, the sulfonated solid catalyst was oven-dried at 80°C for 1 hour and the dried catalyst was packed in airtight plastic bags for the next process. The sulfonated solid carbon catalyst that was prepared at different acid concentration was represented by bamboo



SCHEME 1: Reaction mechanism for converting cellulose into 5-HMF.

carbon with no sulfonation (BC-0), bamboo carbon sulfonated with 98% concentrations of H_2SO_4 (BC-SO₃H₋₁), bamboo carbon sulfonated with 96% concentrations of H_2SO_4 (BC-SO₃H₋₂), and bamboo carbon sulfonated with 94% concentrations of H_2SO_4 (BC-SO₃H₋₃).

2.3. Synthesis, Separation, and Characterization of 5-HMF

2.3.1. Effect of Pretreatments

(1) *Delignification of Corncob*. The delignification process of corncob was carried out by using the method described elsewhere [10]. The corncob powder was soaked into 20% of NaOH solution. The ratio between solid and solution was 1 : 10 (weight/volume). The delignification process was conducted at a temperature of 70°C under vigorous stirring. After the process is completed (12 hours), the treated corncob was separated from the liquid using a vacuum filtration system. The delignified corncob was repeatedly washed with distilled water until the pH of the washing solution reaches around 6.5–7. Subsequently, the treated corncob powder was dried at 110°C for 24 hours and stored in a plastic bag for the next process. The purpose of delignification of the corncob is to expose the cellulose for easy conversion to simple sugars.

2.3.2. *Synthesis of 5-HMF*. The reaction was conducted in round bottom flask batch reactor system. Corncob powder (5 g) was added to the round bottom flask containing sulfonated porous carbon catalyst (0.5 g), 20 wt.% NaCl, and water-ethyl acetate biphasic solvent at ratios of 1 : 2. The flask was equipped with a reflux condenser and the reaction mixture was stirred and heated at the desired temperature of (180°C) for a reaction time (3.1 hours). Then the distillate was collected to the extraction flask.

2.3.3. *Separation and Characterization of 5-HMF*. The organic phase containing 5-HMF layer was separated using a rotary evaporator. The product separated from the solvent was analyzed with FTIR in order to identify attached functional group on 5-hydroxymethylfurfural.

3. Results and Discussion

3.1. *Characterization of Corncob and Catalyst*. In this chapter, the prepared catalyst was characterized by using, FTIR, XRD, SEM, TGA, and elemental analysis. The total acid densities of the catalysts were also measured using back titration and direct titration for SO₃H acid density. The intermediate product synthesized from delignified corncob (5-HMF) was characterized with FTIR spectroscopy.

3.1.1. *Proximate Composition of Corncob*. The proximate analysis of raw corncob (moisture content, volatile matter, fixed carbon, and ash content) was determined using ASTM D1762-84. The measurement was done three times and the average was taken to increase the accuracy.

Table 1 shows the result of proximate analysis of raw corncob. The results were in general agreement with other results reported elsewhere [3, 11, 12]. The low ash content obtained in this study may be due to the use of different corncob species of varieties and treatment conditions [11]. The corncob having higher moisture content needs more heat for moisture vaporization. Ash is a measure of inorganic impurities in the corncob and in this study the low in ash content helps to decrease sludge formation during the synthesis of 5-HMF. Having low moisture content is suggested for the catalytic conversion process due to the fact that high moisture content may increase water content in the reaction, which hinders the catalytic activity of the catalyst by interacting with hydrogen bond of the cellulose of corncob with the water molecule rather than with the catalyst [13].

3.1.2. *Chemical Composition of Corncob*. The chemical composition of corncob was determined using the method described by [14]. Table 2 shows the result of chemical composition of raw corncob and NaOH-treated corncob. The results of this study are in comparable range with values in some literatures reported elsewhere [2, 3, 15]. The low value of lignin content (19.88 w/w%) is important for easy hydrolysis of the hollow-cellulose (cellulose and hemicellulose). Because the corncob contains high cellulose, this material is suitable as the raw material for 5-hydroxymethylfurfural production [10].

TABLE 1: Proximate composition of raw corncob.

Property	Value (wt.%)
Ash content	0.73
Moisture content	5.4
Volatile matter	81.2
Fixed carbon content	12.67

TABLE 2: Chemical composition of raw corncob.

Chemical composition	Corncob (w/w%)	NaOH-treated corncob (w/w%)
Extractives	5.8	3.21
Cellulose	52.64	59.83
Hemicellulose	17.81	17.08
Lignin	23.75	19.88

3.2. Raw Bamboo and Catalyst Characterization

3.2.1. Proximate Analysis of Raw Bamboo Wood. Proximate analysis was required to have information about moisture, volatile matter, and ash as well as fixed carbon contents of bamboo wood. These properties are relevant to the thermal conversion of any biomass material into energy [11]. The proximate analysis of the raw bamboo dust (moisture content, volatile matter, fixed carbon, and ash content) was determined using ASTM D1762-84. The measurement was done three times and the average value was taken to increase the accuracy.

Table 3 shows the proximate analysis results of the raw bamboo. The bamboo sample was high in volatiles and fixed carbon but low in ash content. This high volatile matter content was anticipated because of the organic nature of the material used. The contents of volatile matter in biomass materials are usually high due to the organic nature of the biomass [11]. The bamboo supplied had a moisture content of about 4.6%, which is a well-tolerated value for the production of activated carbon. The proximate analysis reported here is in general agreement with previous studies [16]. Biomass with higher fixed carbon content has higher activated carbon yield and higher surface area for attachment of the sulfonated group during sulfonation reaction. The low ash content would result in minimal effects of inorganic impurities on pore development during activation process. Previous studies suggested that suitable activated carbon should be low in ash but rich in carbon and volatiles [17]. High ash content is undesirable for activated carbon since it reduces the mechanical strength of carbon and affects adsorptive capacity [18].

3.2.2. Ultimate Analysis (CHNS) of the Catalyst. Ultimate analysis is used to determine the elemental composition of the sample. It is based on the principle of Dumas method, which involves the complete and instantaneous oxidation of the sample by flash combustion.

Investigation on ultimate or elemental analysis of the catalyst and bamboo carbon was done and the results are shown in Table 4. The results confirm that the bamboo carbon (BC-0) has higher carbon content than the catalyst

TABLE 3: Proximate analysis of raw bamboo wood powder.

Property	Value (%)
Ash content	1.4
Moisture content	4.6
Volatile matter	80.62
Fixed carbon content	17.98

TABLE 4: Elemental analysis of the catalyst and bamboo carbon.

Sample	N (%)	C (%)	H (%)	S (%)
BC-0	0.15	76.34	3.16	—
BC-SO ₃ H ₋₁	0.25	60.32	2.53	1.87
BC-SO ₃ H ₋₂	0.28	61.21	2.23	1.63
BC-SO ₃ H ₋₃	0.32	63.42	2.61	1.52

(BC-SO₃H₋₁, BC-SO₃H₋₂, and BC-SO₃H₋₃). The elemental analysis also shows that the catalyst prepared by sulfonation of the bamboo carbon with 98% H₂SO₄ has high sulfur content than the catalyst prepared by sulfonation of the bamboo carbon with 96% and 94% H₂SO₄, which agrees with acid density of the catalysts discussed above. In addition to this, the elemental analysis shows that the increase in sulfur content with increasing acid concentration confirms increasing of active sites in the catalyst, resulting in increasing total acid density and catalytic activity. As shown in Table 4, the result shows an increase of nitrogen content with sulfonation. It indicates that the volatilization of nitrogen during sulfonation is very low.

3.2.3. Acid Density of the Catalyst. The total acidity groups, as well as the amount of SO₃H group, were determined by using back titration for total acid density and direct titration for SO₃H acid density following the method reported in the literature [9].

The total acid density and amount of -SO₃H group for the catalyst results are presented in Table 5. The total acid density and amount of -SO₃H group which are incorporated into the carbon were increased as the concentration of the sulfonation agent, H₂SO₄, was increased. As can be seen in Table 5, total acid density and amount of -SO₃H groups were not observed in the carbon without sulfonation.

3.2.4. Fourier Transform Infrared Spectroscopy. The FTIR spectra of the sulfonated solid carbon catalyst, which was prepared at a different concentration of sulfuric acid, are presented in Figures 1(a)–1(d). In Figure 1(a), there is a broad peak between 3600 cm⁻¹ and 3000 cm⁻¹ attributable to aliphatic C-H bond, aromatic C-H bond, O-H bond in a carboxylic acid group, and O-H bond in a phenyl group [19]. An additional peak at 1624 cm⁻¹ was C=O stretching vibration peak.

In Figure 1(b), the occurrence of peaks at 1027–1061 cm⁻¹ was attributed to the symmetric S=O stretching vibration. This band implies the presence of SO₃H groups and confirms the incorporation of sulfonic groups onto the carbon matrix after sulfonation. As seen from Figure 1(a), the aliphatic C-H bond, aromatic C-H bond, O-H bond in a carboxylic acid group, and O-H bond in a

TABLE 5: Total acid density and amount of $-\text{SO}_3\text{H}$, COOH , and OH groups of catalyst.

Sample type	Total acid density (mmol/g)	The amount of $-\text{SO}_3\text{H}$ group (mmol/g)	COOH and OH (mmol/g)
BC- SO_3H_{-1}	3.5	0.61	2.89
BC- SO_3H_{-2}	3.43	0.45	2.98
BC- SO_3H_{-3}	3.28	0.24	3.04

Note: BC-0 is carbon catalyst without sulfonation; BC- SO_3H_{-1} , BC- SO_3H_{-2} , and BC- SO_3H_{-3} are carbon catalysts sulfonated with different concentrations of H_2SO_4 (98%, 96%, and 94%), respectively.

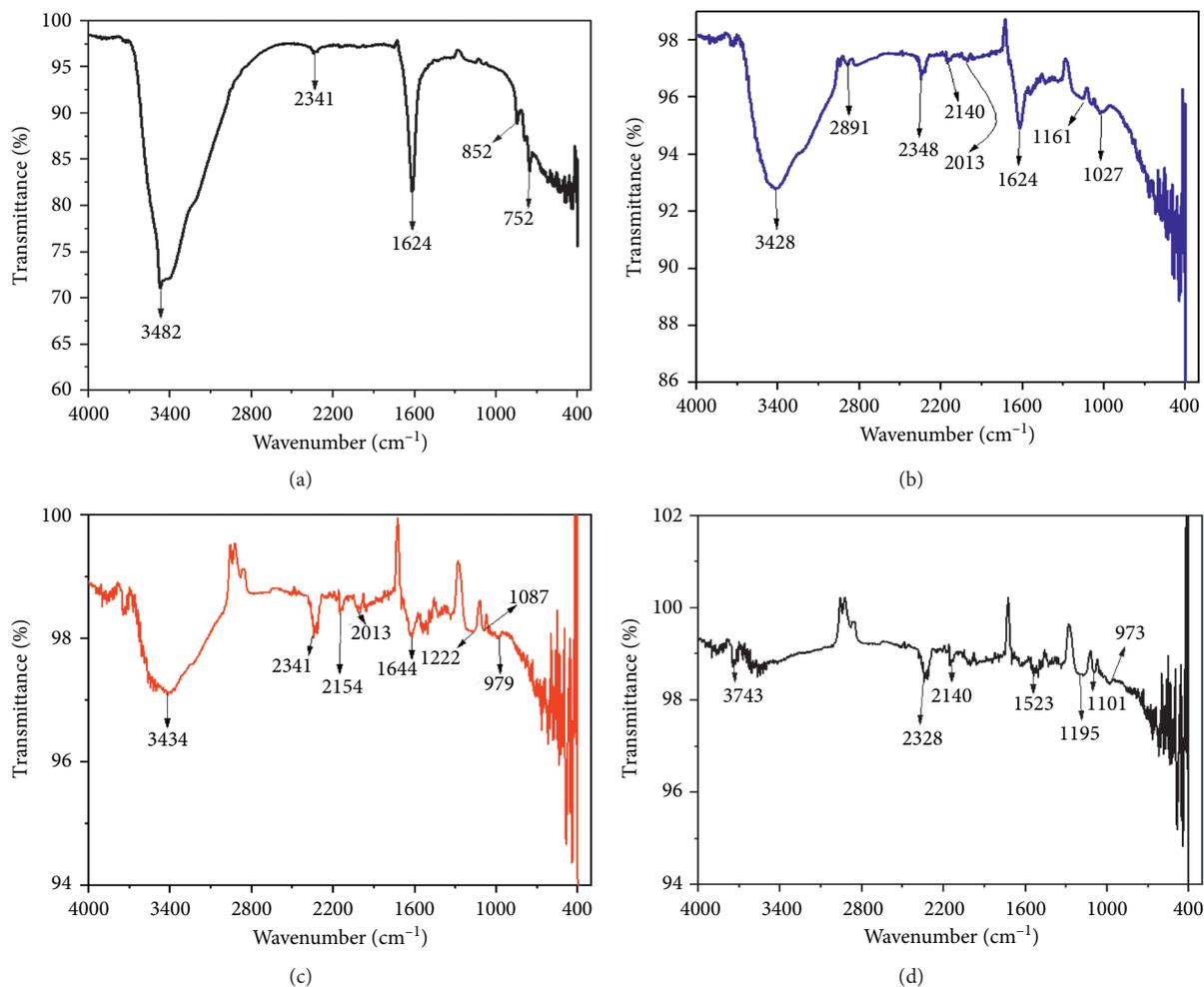


FIGURE 1: FTIR spectrum of sulfonated carbon catalysts (a) BC- 0 , (b) BC- SO_3H_{-1} , (c) BC- SO_3H_{-2} , and (d) BC- SO_3H_{-3} .

phenol group have also been seen in the spectra of BC- SO_3H_{-1} (sulfonated carbon catalyst). The FTIR of BC- SO_3H_{-1} also contains a peak at 1631 cm^{-1} which is assigned to the stretching vibration of $\text{C}=\text{C}$ groups in the aromatic and 1242 cm^{-1} is $\text{C}-\text{O}$ vibration.

Figure 1(c) has weak peaks at 1051 cm^{-1} (symmetric $\text{S}=\text{O}$ stretching) and 1244 cm^{-1} ($\text{C}-\text{O}$) and medium peak at 1658 cm^{-1} ($\text{C}=\text{C}$). From (c), the band intensity that shows the aliphatic $\text{C}-\text{H}$, aromatic $\text{C}-\text{H}$ bond, $\text{O}-\text{H}$ bond in the carboxylic acid group, and $\text{O}-\text{H}$ bond in the spectra becomes weak, which agrees with the fact that an acid density of the catalyst was decreased as the concentration of sulfuric acid decreased from 98% to 96%. The bands that show the present

SO_3H and the aliphatic $\text{C}-\text{H}$, aromatic $\text{C}-\text{H}$ bond, $\text{O}-\text{H}$ bond in the carboxylic acid group, and $\text{O}-\text{H}$ bond in (b) and some amount in (c) are not visible in the FTIR spectrum of (d). This was due to the fact that the total acid density and amount of SO_3H in the sample (d), (i.e., carbon catalyst in which bamboo carbon was sulfonated with 94% H_2SO_4), were much smaller than samples (b) and (c).

The overall FTIR analysis suggests that the carbon-based catalysts consist of polycyclic aromatic carbon sheets containing SO_3H , COOH , and OH moieties, in agreement with the research report for acid-functionalized incomplete carbonized sugars catalyst [4, 20]. From this perspective, we can deduce that as the acid concentration increases for

sulfonation purpose, the total acid density and amount of SO_3H group could increase and affect the reaction medium during the hydrolysis\dehydration process.

3.2.5. X-Ray Diffraction (XRD). The XRD patterns shown in Figure 2 ($\text{BC-SO}_3\text{H}_{-1}$ and $\text{BC-SO}_3\text{H}_{-2}$ and $\text{BC-SO}_3\text{H}_{-3}$) exhibit similar patterns. In both cases, typical crystal diffraction peaks were not seen. The width and weak diffraction peak around $2\theta = 19.46^\circ - 23.34^\circ$ in all patterns implied that the structures of both samples were amorphous. This was due to the fact that the cellulose and hemicellulose chains of branches may dehydrate. Lignin may polymerize or rearrange. Crystal structure decomposed and amorphous hydrocarbon structure was detected.

3.2.6. Thermogravimetric Analysis. The thermal behavior of BC-0 and $\text{BC-SO}_3\text{H}_{-1}$ catalysts was determined by TGA as shown in Figure 3. Thermogravimetric analysis (TGA) was performed in a thermogravimetric analyzer (TA Instruments, SDT Q600 V20.9 Build 20) using temperature programming from 35 to 800°C at the heating rate of $20^\circ\text{C}/\text{min}$ to which the sample was heated under a 2 mL/min flow of nitrogen. The TGA result of bamboo carbon in Figure 3 indicates that the initial weight loss begins at a temperature around 55°C . The weight loss of the carbon-based catalysts sample can be associated with the decomposition of the functional groups as well as the carbon structure. Weight loss at $100-125^\circ\text{C}$ is associated with the evaporation of moisture for bamboo carbon. Similarly, the marginal weight loss occurred for sulfonated catalyst ($\text{BC-SO}_3\text{H}_{-1}$) sample at $100-125^\circ\text{C}$ due to desorption of water vapors. From 135 to 440°C , there was a steady change in weight percentage of bamboo carbon. From 440 to 800°C for BC-0, a continuous weight loss can be observed from a plot which refers to thermal decomposition of weak acidic sites and strong Bronsted acidic sites [21]. For the overall analysis, the sample lost about 8% of its weight at 800°C .

For sulfonated carbon catalyst, it can be observed that it can bear temperatures up to 465°C ; as can be seen from the plot, the weight of the catalyst drops slightly plateaued from 125 to 465°C , which can be interpreted to be due to the decomposition of the SO_3H groups. For sulfonated carbon catalyst, loss of weak and strong Bronsted acidic sites was observed to be from 465 to 800°C .

3.2.7. Scanning Electron Microscopy (SEM). The morphology and surface structure of the carbonized bamboo dust after sulfonation are shown in Figure 4. Scanning electron microscopy (SEM) has been extensively used to characterize the microstructure of bamboo carbon and sulfonated bamboo carbon catalyst. The surface morphology, such as the surface shape, pattern, and feature of the selected bamboo carbon and sulfonated carbon catalyst, was observed using JEOL JSM-IT300 SEM attached with Energy Dispersive X-ray (EDX).

SEM images for both BC-0 and $\text{BC-SO}_3\text{H}_{-1}$ catalyst suggested that the white dots represent the inorganic composition [21]. It can be revealed from the images that

activated carbon possesses irregular compact structure, while sulfonated catalyst particles appear to be like smooth surfaces. From these images, it can be seen that the sulfonated catalyst ($\text{BC-SO}_3\text{H}_{-1}$) consisted mainly of aggregates of carbonaceous micropores that had diameters of several μm . The white spots of the mesoporous catalyst were partially destroyed after treatment through sulfonation. When bamboo carbon was sulfonated with H_2SO_4 , a morphological change occurred and the resulting bamboo carbon sulfonated catalyst had micropores due to sulfonation. It is believed that, during the sulfonation process, the carbon tubes, which are not strongly bound, are arranged into amorphous carbon or burnt away [22]. The morphological difference between the catalyst and bamboo carbon implies the incorporation of $-\text{SO}_3\text{H}$ in bamboo carbon.

3.3. Performance of $\text{BC-SO}_3\text{H}_{-1}$ Catalyst for Conversion of Corncob to HMF. Further investigation on the activity of the catalyst was performed in the synthesis of HMF from corncob. The synthesized activated and sulfonated carbon catalyst was utilized for synthesis of HMF. Based on the acid density, elemental analysis, and FTIR analysis, the best catalyst ($\text{BC-SO}_3\text{H}_{-1}$) was chosen for suitable conversion of corncob to HMF. The hydrolysis\dehydration reaction was carried out using a 250 ml capacity round bottom flask reactor which was equipped with a condenser, magnetic stirrer, and temperature probes. The magnetic stirrer's rotational speed, reaction time, and temperature were adjusted to the desired conditions. The result obtained was confirmed via FTIR test.

3.3.1. Characterization Results of the Intermediate Product Using FTIR. The product was characterized and confirmed by using FTIR spectroscopy. Samples were measured on Spectrum 65 FTIR (PerkinElmer) in the range of $4000-400\text{ cm}^{-1}$ using unwarped salt plates. The HMF's characteristic FTIR absorptions were associated with the $-\text{OH}$, C-H , $\text{C}=\text{C}$, and $\text{C}=\text{C-H}$ stretching vibrations. Figure 5 depicts FTIR spectra of HMF that was synthesized from corncob using solid sulfonated carbon catalyst. FTIR spectrum of HMF appeared as broader and sharper bands in the region. These bands are attributed to the presence of free alcoholic O-H groups stretching vibration at $3,400\text{ cm}^{-1}$ in 5-HMF, aldehyde C-H at $2,850$ and $2,930\text{ cm}^{-1}$, aldehyde $\text{C}=\text{O}$ stretching at $1,675\text{ cm}^{-1}$, aromatic $\text{C}=\text{C}$ stretching at $1,520\text{ cm}^{-1}$, and furan ring ether asymmetric stretching C-O-C at $1,190\text{ cm}^{-1}$, which was confirmed by [23]. The band at $1,667\text{ cm}^{-1}$ and $1,221\text{ cm}^{-1}$ indicates the presence of carbonyl group ($\text{C}=\text{O}$) and carbon-carbon double bond ($\text{C}=\text{C}$), respectively, and alcoholic C-O stretching at $1,025\text{ cm}^{-1}$ was observed [24]. The peaks between $1,700$ and $1,500\text{ cm}^{-1}$ are associated with $\text{O-C}=\text{CH}$ sites on the furan ring, respectively, and are attributed to a heterocyclic aromatic compound, furan, indicating the presence of HMF aromatic rings [25]. Also, the stretching vibration between $1,400$ and 900 cm^{-1} indicates the C-C-H , C-O-H , and O-C-H of the furan ring [26]. This assures that the product obtained from corncob was HMF due to the confirmation of these regions as shown in Figure 5.

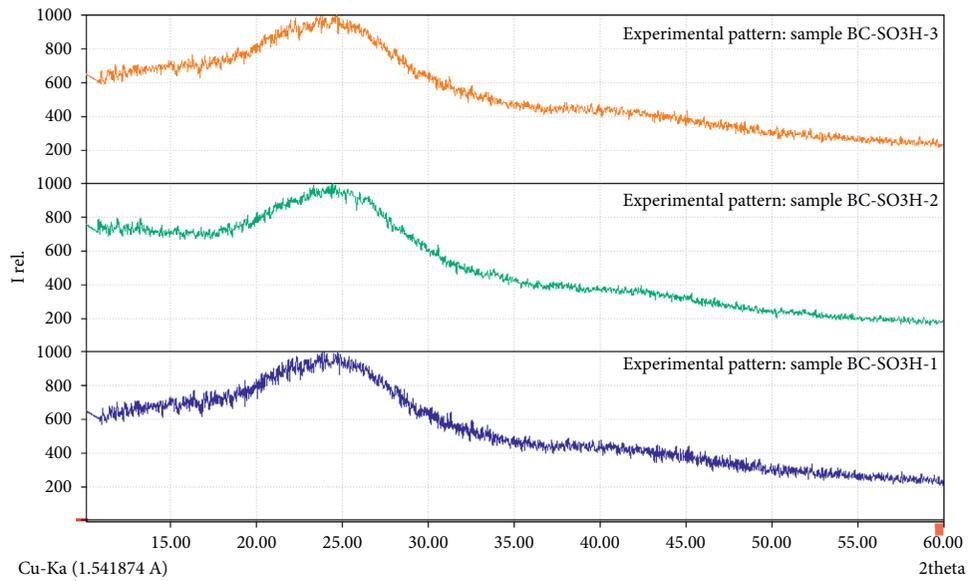


FIGURE 2: XRD pattern of catalyst prepared by (a) 98%, (b) 96%, and (c) 94% H_2SO_4 .

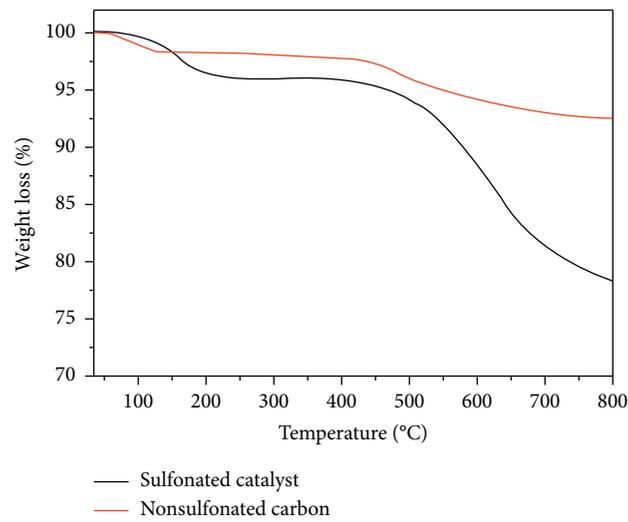


FIGURE 3: Thermogravimetric analysis (TGA) for catalyst from bamboo wood powder carbonized at $450^\circ C$ BC-0 and after sulfonation (BC-SO₃H₁).

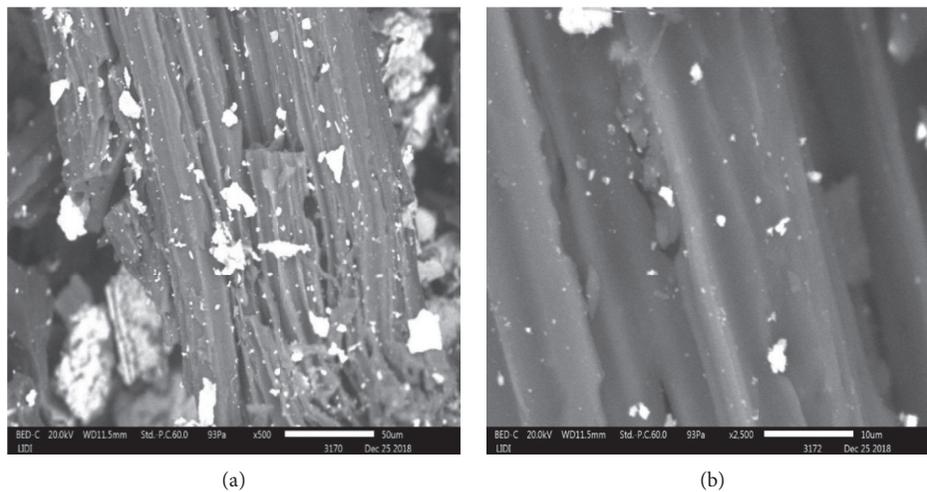


FIGURE 4: SEM image of (a) BC-0 and (b) BC-SO₃H₁.

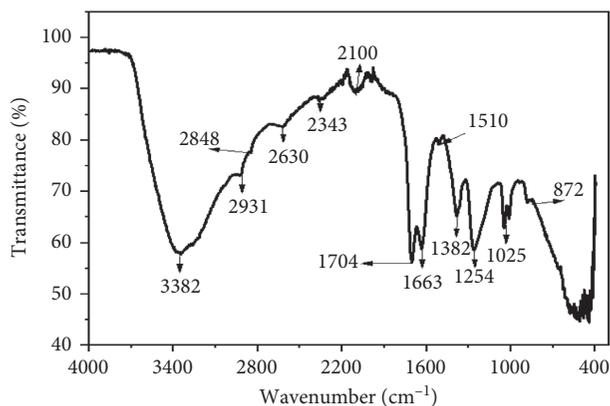


FIGURE 5: Characterization results of the intermediate product using FTIR.

4. Conclusion

Corn cob had been successfully used as potential raw material for 5-HMF synthesis. The synthesis of 5-HMF was conducted in hydrolysis-dehydration reaction conditions with the presence of acid modified bamboo wood carbon catalyst. The reaction was intensified with water-ethyl acetate as a biphasic solvent by addition of NaCl in the reaction medium for the purpose of creating an interface between the organic and water phases. The catalyst was synthesized from bamboo with zinc chloride as textural promoter and resulted in high acid density carbon-based catalyst using a pyrolysis and sulfonation method. Structural study through elemental analysis and FTIR spectroscopy suggests that biochar-based catalyst consists of polycyclic aromatic carbon sheets bearing three different acidic groups of phenolic (OH), carboxylic (COOH), and sulfonic (SO₃H), and the catalyst is stable up to temperature of 465°C. In general, with increasing sulfuric acid concentration, the total acid density of the catalyst also increases due to high availability of sulfonic group.

Data Availability

All the necessary information required for replication of this work and/or conducting secondary analysis is included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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