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Synthesis and evaluation of carbon-based solid catalyst from sugar bagasse biochar for selective conversion of fructose to 5-HMF

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Abstract. A carbon-based solid acid catalyst was prepared from sugar bagasse via calcination and subsequent sulfonation. The structural and surface properties of the solid acid catalyst were evaluated via X-ray Diffraction (XRD), Ammonia Temperature-Programmed Desorption (TPD-NH_3), Fourier-transform infrared spectroscopy (FT-IR), and Brunauer–Emmett–Teller (BET) measurements. The results showed that the catalyst has an amorphous carbon structure with a surface area exceeding 750 m^2/g, an acid density of approximately 10.65 mmol/g, a pore size distribution in the range from 2.5 to 2.9 nm and strong acid sites of -SO_3H. The X-ray Photoelectron Spectroscopy (XPS) analysis showed a high content of functional groups on the surface of the catalyst. The 5-Hydroxymethylfurfural (5-HMF) was synthesized from fructose using the catalyst. High-performance liquid chromatography (HPLC) quantified 5-hydroxymethylfurfural (5-HMF) yields, while gas chromatography-mass spectrometry (GC-MS) identified reaction intermediates and byproducts formed during catalytic biomass dehydration. The effect of reaction time on fructose conversion and 5-HMF selectivity was assessed. At a reaction time of 2.5 h, 100 % of fructose was converted into the 5-HMF with a selectivity of 93.22 %.

Keywords: 5-HMF, carbon-based solid acid catalyst, fructose, sugar bagasse.

Classification numbers: 2.1.3.

1. INTRODUCTION

5-hydroxymethylfurfural (5-HMF) is one of the promising biomass-derived platforms [1–4]. This compound can be used to synthesize 2,5-furandicarboxylic acid (FDCA), a potential renewable crosslinker consisting of a furan ring at its core and two carboxylic acid groups. FDCA has garnered notable attention as a viable substitute for terephthalic acid (TPA), a widely used petrochemical monomer, in the production of comparable biobased polymer [5]. Additionally, the 5-HMF finds another application in the production of polyethylene 2,5-furandicarboxylate (PEF) as a replacement for the commonly employed petroleum-based polymer, polyethylene terephthalate (PET), serving the same purpose [6].

Acid-catalyzed dehydration is the primary method for producing 5-HMF from sugars. Among available raw materials, fructose is the most convenient and effective starting point because its fructofuranose ring structure exhibits exceptionally high reactivity toward dehydration. As a result, researchers routinely use fructose as a model substrate to test and evaluate the efficiency of new catalytic systems in biomass conversion [7–9].

There are many studies using fructose as a raw material for the 5-HMF synthesis because of high 5-HMF yields and selectivity [10–13]. Combined with the isomerization of glucose to fructose, a two-stage synthesis of the 5-HMF is potentially more efficient than direct synthesis of the 5-HMF owing to the higher abundance and significantly lower cost of glucose compared to fructose [14, 15].

Fructose dehydration yields 5-HMF via partially dehydrated intermediates. However, side reactions can occur: the intermediates can polymerize into humins, and 5-HMF can rehydrate into levulinic acid. To maximize 5-HMF yield, catalyst design must focus on accelerating intermediate dehydration while minimizing product hydrolysis.

Recently, researchers have focused on exploring and utilizing solid acid catalysts for the dehydration process. Regarding the preparation methods, utilizing biomass as a renewable, abundant, and cost-effective resource offers potential advantages for the direct production of carbon-based solid acid catalysts. These advantages include good reusability, non-causticity, and environmental friendliness, as well as production from renewable lignocellulosic material sources [11, 12, 16]. In comparison to alternative solid acids, CBSC offers distinct benefits that include facilitating streamlined processes for product separation and purification, minimizing the generation of waste, and alleviating concerns related to catalyst disposal and equipment corrosion. Moreover, in terms of the CBSC applications, the utilization of high surface area and porous carbon materials of various diameters facilitates enhanced contact between reactants and catalytic active sites, resulting in high catalytic activity and catalytic selectivity [11, 12, 17–20]. Besides, it is imperative to conduct further investigations aimed at enhancing the catalytic stability and mechanical strength of CBSC.

Huang and his colleagues successfully demonstrated the efficient conversion of microalgal lipids into biodiesel at room temperature with a remarkable yield of 96.8 % [21]. This achievement was made possible through the utilization of a newly developed biomass-derived SO_3H-functionalized graphene-like photothermal catalyst, known as S-NGL-600, under light irradiation. Significantly, the photothermal catalyst exhibited outstanding recyclability and outperformed the industrially used catalyst H_2SO_4 in terms of microalgal lipid conversion rate. Furthermore, a life cycle assessment revealed energy-saving benefits (0.87 MJ/MJ) and environmental advantages (–89.42 CO_2eq/MJ) of the photothermal-driven approach for microalgal biodiesel production.

In a separate investigation conducted by Huang *et al.*, a layered 3D structure PAP-MEPP-C) biochar catalyst with controllable acidity was synthesized through low-temperature carbonization (80 °C) of monomers derived from lignin [22]. The developed PAP-MEPP-C biochar catalyst exhibited notable catalytic activity in the conversion of Jatropha oil with varying acid values ranging from 17.9 to 155.4 mg KOH/g. This exceptional performance was attributed to the unique layered 3D structure and abundant acidity (5.33 mmol/g) from the -SO_3H groups, which facilitated optimal contact (174.4 m^2/g) between the reactants and the acidic sites. The study achieved a remarkable maximum biodiesel yield of 97.2 %. Furthermore, the investigated biochar catalyst exhibited high stability, allowing for four consecutive recycling cycles with a biodiesel yield exceeding 90 %.

Charinpanitkul and co-authors synthesized sulfonated magnetic carbon nanoparticles (SMCN) from eucalyptus oil [11]. The experimental results showed a fructose conversion rate of 84 % and a 5-HMF yield of 51.6 % at a reaction temperature of 180 °C, a reaction time of 30 mins, and a catalyst-to-fructose mass ratio of 0.167. SMCN catalysts exhibit the ability to sustain their catalytic efficiency for up to three cycles without experiencing a notable decline. The environmentally conscious synthesis of SMCNs from renewable carbon feedstocks, coupled with their impressive reusability, has the potential to facilitate the eco-friendly production of platform chemicals. However, high-temperature reactions in this work pose disadvantages related to the formation of humic substances. These by-products adhere to the catalyst surface in the presence of water, thereby reducing the catalyst's activity and reusability [23, 24].

Douyong Min and his associates prepared lignin-based carbon solid acid catalyst via the sulfonation of lignin-based activated carbon solid with sulfuric acid [12]. Under the recorded optimum conditions (reaction temperature of 170 °C, reaction time of 60 mins, catalyst dosage of 30 mg/mL, and fructose concentration of 20 mg/mL), the yield of 5-HMF obtained was 75.7 % in dimethyl sulfoxide media. After undergoing five consecutive recycling cycles, the catalyst demonstrated a noteworthy recovery rate surpassing 95 %, while achieving a yield of the 5-HMF exceeding 70 %. This outcome carries substantial implications for cost reduction of catalysts and mitigation of environmental pollution, as the process excludes the utilization of mineral acid catalysts. In this work, XPS was used to characterize the catalyst. However, the XPS analysis was solely used to confirm the successful sulfonation process without considering the surface functional groups possibly present in the catalyst.

In our previous work, the CBSC was prepared from acacia mangium wood sawdust via H_3PO_4 impregnation followed by sulfonation [25]. Under the optimized conditions, the obtained catalyst had a total acid site density of approximately 5.08 mmol/g and a specific surface area of 740 m^2/g. Catalyst characterization by FT-IR method showed the formation of surface functional groups, such as -OH, -COOH, and C=O groups. The presence of these oxygen functional groups created hydrophilicity for the hydrophobic carbon structure of porous carbon and CBSC material, which promoted reactant access to $-SO_3H$ active sites while preventing the immediate poisoning of catalyst [26]. In addition, the acidity, whether weak or strong, of these groups also led to the effective catalytic performance of the CBSCs. However, the FT-IR analysis method employed only confirmed the presence of oxygen functional groups but did not quantify them in the CBSC samples.

Numerous publications have reported on the utilization of carbon solid acid catalysts for the synthesis of 5-HMF [27–30], whose notable advantages arise from the presence of surface oxygen groups, which confer hydrophilic characteristics to the catalyst and facilitate the efficient dispersion of the active species onto the $-SO_3H$ sites. This enhanced dispersion significantly accelerates the desired reaction. The previous publications solely employed FT-IR analysis to confirm the presence of surface oxygen groups, predominantly $-HSO_3$ groups, without quantifying them [27, 28, 30], while some others utilized XPS analysis to confirm the presence of particular specialized functional groups [27].

This study focuses on the preparation of CBSC from sugar bagasse as a catalyst for the selective conversion of fructose into the 5-HMF. The synthesis process involved impregnating the sugar bagasse with an acidic aqueous solution, followed by carbonization to obtain the CBSC. The catalytic performance of CBSC in the conversion of fructose into 5-HMF was evaluated using temperature-programmed desorption of ammonia (TPD-NH_3) analysis to

determine the catalyst's acidity. The structural characterization of the carbon material and catalyst was conducted through X-ray diffraction (XRD) and Fourier transform infrared (FT-IR) spectroscopy. The X-ray photoelectron spectroscopy (XPS) was employed to investigate surface functional groups, while the catalyst's performance in the 5-HMF synthesis reaction was assessed using high-performance liquid chromatography (HPLC) and gas chromatography-mass spectrometry (GC-MS). Notably, the innovative aspect of this study lies in the quantitative analysis of surface oxygen groups using the XPS method, which provides valuable insights into their abundance and facilitates a deeper understanding and advancement of this research area.

2. MATERIALS AND METHODS

2.1. Materials

Air-dried sugar bagasse (Lam Son Sugar Cane JSC, Thanh Hoa, Vietnam) was stored at room temperature in sealed containers. All analytical-grade reagents, including D-(-)-Fructose (CAS: 57-48-7, ≥ 99 wt.%), phosphoric acid (CAS: 7664-38-2, ≥ 85 wt%), sulfuric acid (CAS: 7664-93-9, 98 %), and DMSO (CAS: 67-68-5, ≥ 99.9 %), were purchased from Sigma-Aldrich and used without further treatment.

2.2. Methods

2.2.1. Preparation of catalysts

Carbon-based solid acid catalysts were synthesized following a modified literature procedure [25]. Briefly, sugar bagasse (100 g) was impregnated with 300 mL of 25 % (w/w) aqueous H_3PO_4 at 50 °C for 30 min, separated, and air-dried. The precursor was carbonized in a tube furnace under argon flow (25–450°C at 2.0 °C min^{-1}, held for 1 h), ground, washed with hot water to neutral pH, and dried at 105 °C. For sulfonation, 10 g of the carbon was heated with 50 mL of concentrated H_2SO_4 (98 %) at 100 °C for 5 h in a closed flask. The mixture was ice-cooled, added to 400 mL of distilled water, and the resulting precipitate was washed with hot distilled water until neutral before drying at 105 °C.

2.2.2. Catalyst characterization

Surface area, pore parameters (size distribution, average radius, total volume) for 0.1 g samples, and acid density were determined via N_2 adsorption-desorption (Gemini VII 2390 and ASAP 2020 V4.03) and TPD-NH_3 (2920 analyzer), respectively; all samples were priorly degassed at 120 °C (under helium for TPD) to prevent burning. Structural characterizations employed XRD (Cu-Kα, λ = 0.1540 nm, 40 kV, 30 mA, 2θ = 5° – 80°) and FT-IR (Thermo Nicolet 6700 NRX with Raman Module, 4000–400 cm^{-1}). XPS (ESCALAB 250Xi, Thermo Fisher Scientific, USA; Al Ka) utilized narrow sweeps for semi-quantitative analysis, with binding energies calibrated to the C_{1s} peak at 284.8 eV.

2.2.3. Conversion of fructose into 5-hydroxymethylfurfural

Fructose (1 g) and sugar bagasse CBSC catalyst (50 mg, 5 wt.%) were reacted in 10 mL of DMSO (50 mL flask, reflux condenser, 350 rpm) in a 100 °C glycerol bath for 0.5–4 h. The cooled mixture was filtered through filter paper-with the recovered catalyst washed using hot distilled water and dried at 105 °C for recycling-and subsequently through a 0.2 µm syringe filter (Thermo Scientific™ F251317). The liquid filtrate was analyzed via GC-MS and HPLC (Agilent 1200; UV detector at 284 nm; Agilent Eclipse XDB-C18 column at 25 °C;

methanol/water 20/80 v/v mobile phase at 0.6 mL/min; Agilent 2D LC ChemStation Software G2170BA). Fructose conversion and 5-HMF selectivity were calculated based on initial/residual fructose amounts and actual/theoretical 5-HMF quantities, respectively.

3. RESULTS AND DISCUSSION

3.1. Catalyst characterization

3.1.1. XRD and BET

The specific surface area and total pore volume of the carbon materials and the catalyst are summarized in Table 1. The carbon-based solid acid catalysts with specific surface area lower than 2 m^2/g were reported to have poor catalytic activities [31]. Therefore, this research focused on synthesizing a catalyst from sugar bagasse with a large specific surface area to ensure good accessibility to the active sites. The carbon material obtained from carbonization without a prior H_3PO_4 impregnation step had a very low specific surface area (1.79 m^2/g). Compared to nonactivated carbon material, the activated sample had a higher specific surface area (793.52 m^2/g). After sulfonation, the surface area of the carbon material decreased from 793.52 to 754.19 m^2/g. The observed decrease in the surface area of the catalyst, compared to activated carbon, can be attributed to a carbon deposition process, followed by -SO_3H functionalization. This process led to the occupation of some vacant pores within the catalyst. Meanwhile, the total pore volume decreased from 0.268 to 0.060 cm^3/g, which was potentially a result of the changes in pore diameter during sulfonation (from 3.0-9.3 nm to 2.5-2.9 nm). This phenomenon could be attributed to the higher degree of carbonization and the thinning of macropore walls at elevated temperatures, which can lead to the susceptibility of certain macropores to collapse. Besides, the collapse of specific macropores resulted in the formation of additional voids between the fragmented sections, thus lowering the total pore volume.

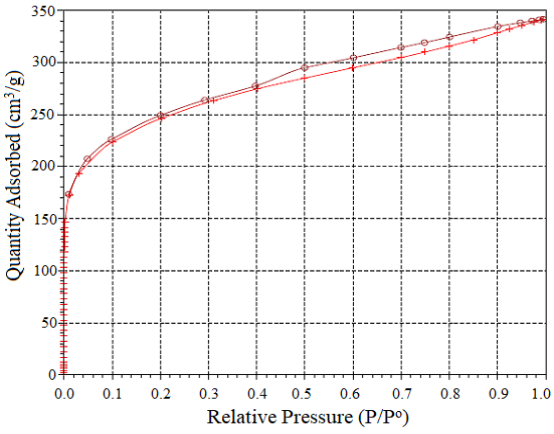


Figure 1. Linear plot of the N_2 adsorption isotherm for the activated carbon material.

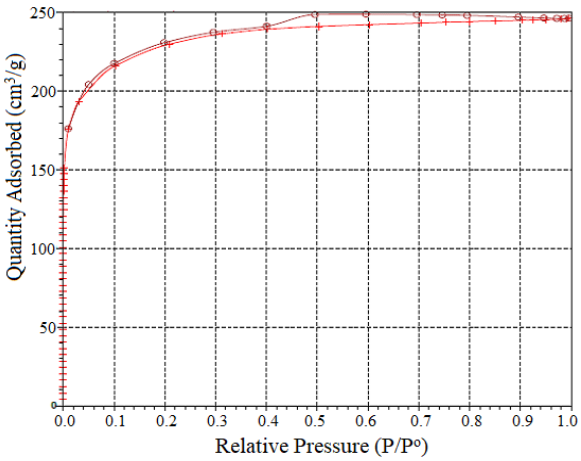


Figure 2. Linear plot of the N_2 adsorption isotherm for the catalyst.

Table 1. Specific surface area and total pore volume of the carbon materials and the catalyst.

Sample	Specific surface area (m^2/g)	Total pore volume (cm^3/g)	Pore diameter (nm)
Nonactivated carbon	1.79	0.006	14.9-115.6

H_3PO_4 activated carbon	793.52	0.268	3.0-9.3
Catalyst	754.19	0.06	2.5-2.9

Linear plots of N_2 adsorption isotherms for the carbon materials before and after sulfonation are shown in Figures 1 and 2, both have a hysteresis loop in the relative pressure range of about 0.4-1, which is type IV, typical for mesoporous materials. However, the carbon material after sulfonation shows characteristics of a more microporous material, clearly evidenced by the similarity to the H4 hysteresis loop depicted in Figure 2.

Figure 3 shows the XRD patterns of carbon material and the catalyst. The results indicate that the materials possess an amorphous carbon structure, characterized by a broad C (002) diffraction peak at a 2θ value of approximately 24°.

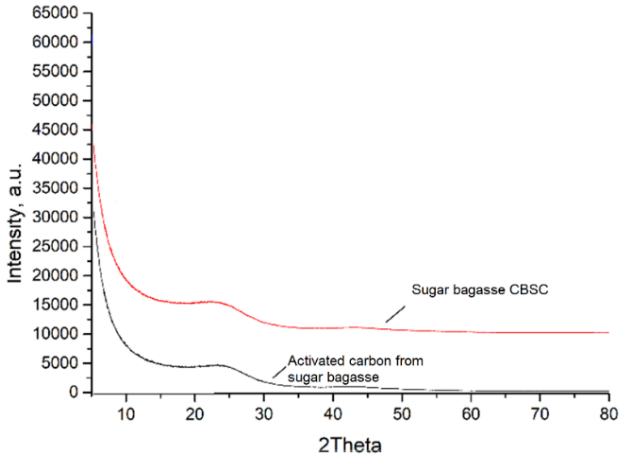


Figure 3. XRD patterns of the carbon material and the catalyst.

3.1.2. TPD-NH_3, FT-IR and XPS

The results of TPD-NH_3 analysis showed that the acidity of as-obtained catalyst samples was 10.65 mmol/g of total acid site density, including 0.63 mmol/g of super strong acid site (897.6 °C), 8.45 mmol/g of very strong acid site (526.6 °C), 1.29 mmol/g of strong acid site (386.9 °C), and 0.28 mmol/g of weak acid site (170 °C) (Figure 4). Compared to other carbon-based solid acid catalysts previously reported [12, 20, 25, 32–35], the catalyst obtained in this work possessed a much higher density of acid sites.

The acid sites of sulfonated carbon-based catalyst were contributed by -SO_3H, -COOH, and -OH groups, which can be observed by FT-IR spectroscopy. The FT-IR spectra of the catalyst shown in Figure 5. The peaks around 1035 cm^{-1} correspond to -SO_2 symmetric and 1176 cm^{-1} correspond to -SO_2 asymmetric stretching vibrations of -SO_3H [33]. This indicates that -SO_3H groups had successfully attached to the activated carbonized materials via sulfonation. The bands at around 3135 cm^{-1} the spectra assign to stretching vibrations of –OH groups in –COOH or phenolic compounds. In addition, the peaks at 1707 cm^{-1} are attributed to the C=O stretching vibration.

Under the same preparation conditions, both the catalyst sample from sugar bagasse in this work and the catalyst sample from wood sawdust in our previous work had a high acid site density. However, there was a significant difference in quantity, with values of 10.65 mmol/g

and 5.08 mmol/g, respectively. This indicates a difference in the content of functional groups on the surface of the catalysts.

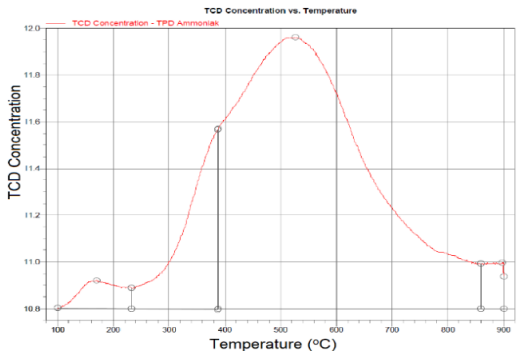


Figure 4. TPD-NH_3 analysis of the catalyst.

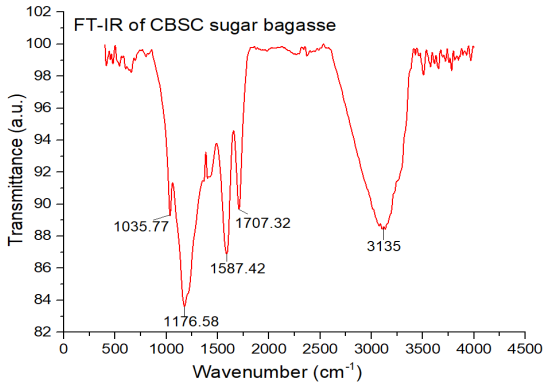
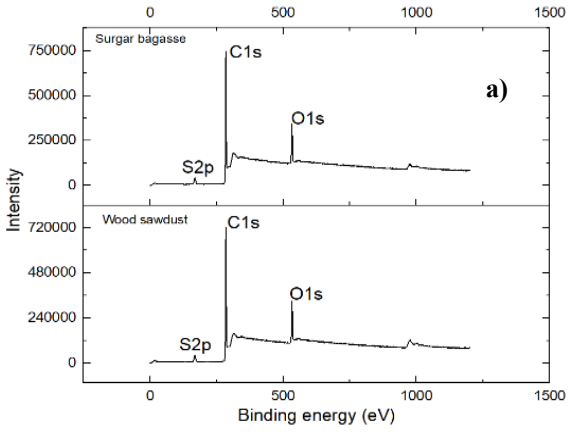
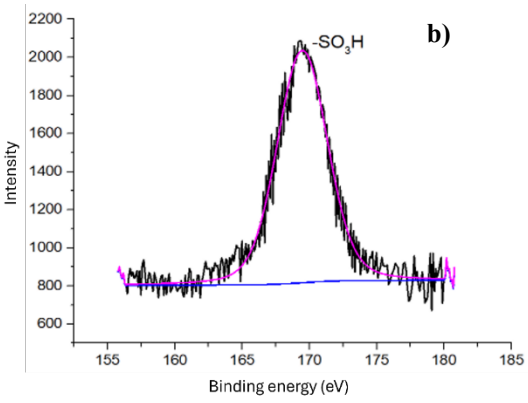


Figure 5. FT-IR spectra of the catalyst.

The XPS analysis method was used to quantitatively determine the functional groups present in the catalyst samples. The XPS results for the samples are shown in Figure 6, and the contents of the functional groups are listed in Table 2. The peaks were deconvoluted using Casa XPS software (v.2.3.15 rev1.3), and the content of functional groups was calculated based on the results of the C_{1s} XPS peak deconvolution.

For all CBSC samples, the C_{1s} spectrum was deconvoluted into five distinct component peaks (Figures 6c and 6d), including C-C and/or C=C at 284.2-284.6 eV, C-O of phenols, ethers or alcohols at 285.8-286.4 eV, C=O of carbonyls, quinones at 287.0-287.4 eV, carboxylic groups at 288.6-289.0 eV, and C-SO_3H at 290.0-290.5 eV [32, 34, 35]. A single pick at around 169 eV appearing in the XPS spectra of the samples, as shown in Figures 6a and 6b, confirmed the presence of SO_3H groups on the surface of the CBSCs.





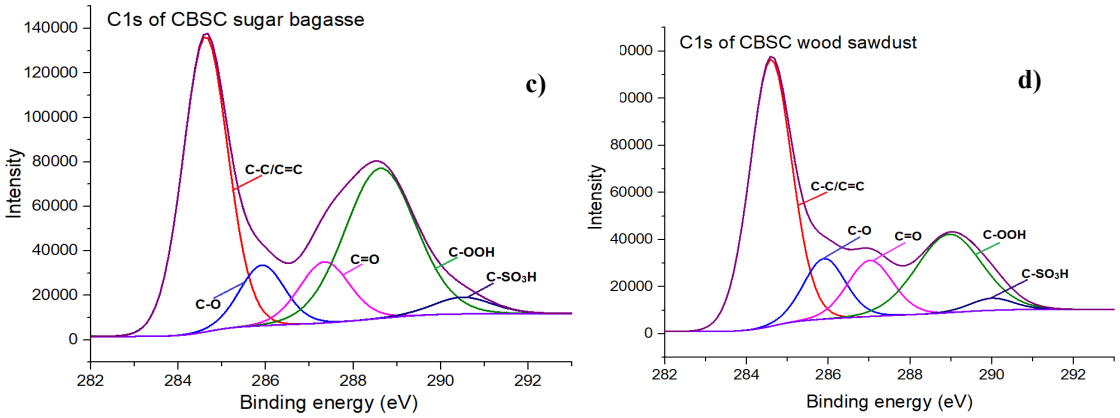


Figure 6. XPS spectra of sugarcane bagasse CBSC and wood sawdust CBSC (a), deconvoluted high-resolution S2p XPS spectra (b), C1s XPS spectra of sugarcane bagasse CBSC (c), and wood sawdust CBSC (d).

It is well known that oxygen functional groups, such as phenol and carboxylic groups, contribute to the acidity of the CBSC catalyst. The results in Table 2 show negligible difference in the content of phenols, ethers, or alcohols groups between the two catalysts, which explains the similarity of weak acid sites of the catalysts. The content of carboxylic groups in the sugarcane bagasse CBSC was 34.83 %, much higher than the content of 15 % in the wood sawdust CBSC; the content of C-SO_3H groups in the sugarcane bagasse CBSC was also higher than that in the wood sawdust CBSC, at 3.15 % and 2.37 %, respectively. These results are consistent with the higher content of very strong acid sites on the sugarcane bagasse CBSC compared to the wood sawdust CBSC.

Table 2. Content of surface function groups of CBSCs obtained from XPS method and acidity by TPD-NH_3 of sugarcane bagasse CBSC compared with wood sawdust CBSC from our previous work [25].

Component	Sugar bagasse CBSC				Wood sawdust CBSC			
	Peak position (eV)		Content (%)		Peak position (eV)		Content (%)	
C-C and/or C=C	284.62		43.13		284.59		51.06	
C-O	285.92		8.89		285.90		11.55	
C=O	287.34		9.99		287.02		11.53	
C-OOH	288.62		34.83		288.96		23.49	
C-SO_3H	290.50		3.15		290.00		2.37	
Quantity of acid sites (mmol/g)	Weak	Strong	Very strong	Super strong	Weak	Strong	Very strong	Super strong
	0.28	1.29	8.45	0.63	0.24	1.26	3.2	-

3.2. Fructose conversion

The catalytic conversion of sugars into 5-HMF is complicated due to side reactions, such as the formation of humic substances and the hydration of 5-HMF into levulinic acid. High reaction temperatures can promote the conversion of fructose but simultaneously reduce selectivity for 5-HMF. The fructose conversion at 170 °C was 98.0 %, while the 5-HMF selectivity was 75.7 %; at 180 °C fructose conversion was 84 %, while the 5-HMF selectivity was 51.6 % [11]. The formation of by-products such as humic substances also reduces the

efficiency of catalyst reusability because these compounds adhere to the catalyst surface. In this work, low-temperature conversion reactions were studied with the aim of preventing the formation of by-products and enhancing the yield of 5-HMF synthesis. In addition, this also contributes to a reduction in the energy expended in converting fructose into 5-HMF.

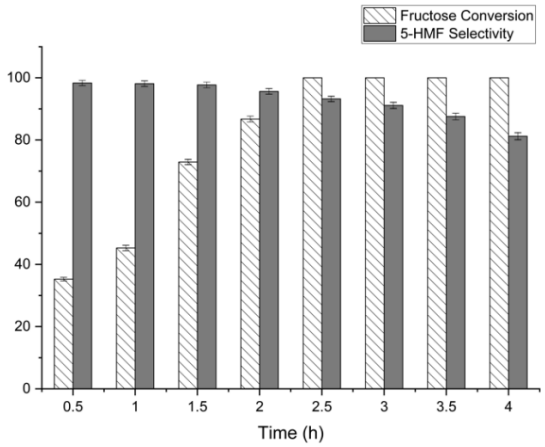
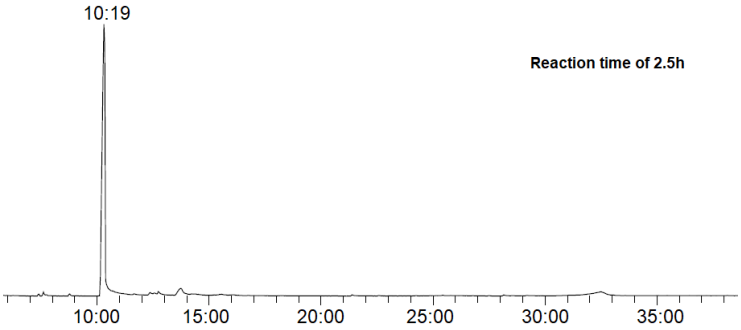


Figure 7. Fructose conversion and yield of 5-HMF selectivity at different reaction times.

The effect of reaction time on the fructose conversion and yield of 5-HMF catalysed by acidic sugar bagasse biochar (at 100 °C and a catalyst dosage of 5 %) is shown in Figure 7. The results showed that with a reaction time of 0.5 h, the conversion of fructose was 35.26 %, and the fructose conversion increased with increasing reaction time; by the reaction time of 2.5 h, 100 % of fructose was converted. With a reaction time of 0.5 h, the selectivity of 5-HMF was 98.34 %, and the selectivity was inversely proportional to reaction time. After 4 h, the selectivity of 5-HMF was 81.22 %. Thus, when the reaction was conducted at a low temperature (100 °C) and in DMSO media, the formation of by-products was minimized. The results also demonstrate that the obtained product 5-HMF can be simultaneously converted to other products. With a reaction time of 2.5 h, 100 % of fructose was converted with the highest 5-HMF selectivity of 93.22 %. The underlying cause can be attributed to the significant surface area and large pore size of CBSC, facilitating the unrestricted movement of reactant and product molecules between the reaction solution and the catalyst surface.

Figure 8 shows GC-MS spectra of the obtained liquid after reaction times of 2.5, 3.5, and 4 h. The number of by-products formed from 5-HMF increased when the reaction time was higher than 2.5 h.



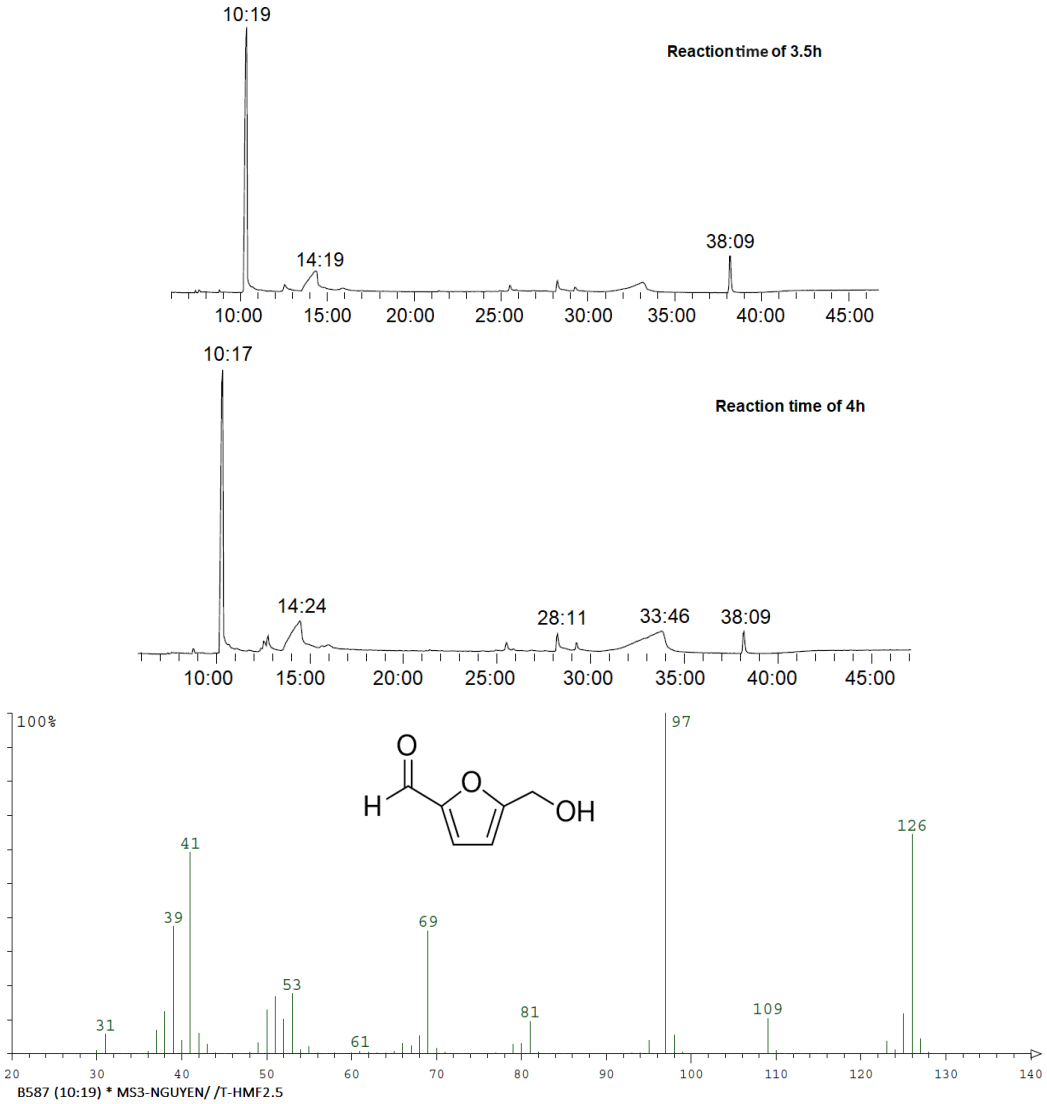


Figure 8. MS spectra of 5-HMF at different reaction times.

Table 3. Comparison of carbon solid catalyst properties and results.

Catalyst	Catalyst characterization				Conversion (%)	Selectivity (%)	Refs.
	-SO3H group (mmol/g)	S_{BET} (m^2/g)	V_P (cm^3/g)	D_s (nm)			
Sugar bagasse CBSC	10.65	754.19	0.06	2.5-2.9	100	93.22	This work
Wood sawdust CBSC	5.08	739.67	-	3-9.3	100	64	[25]
Sulfonated carbons with hierarchically ordered pores (SCHOP-500)	1.30	181	-	4.8	96.1	93.4	[30]
Sulfonic acid-	-	-	-	-	98.7	89.4	[29]

functionalized ordered mesoporous carbon							
Carbon coated acid-activated red mud (AD-1:1/SO_3H)	6.8	69.23	-	6.84	93.05	51.5	[27]
Sulfonic acid-functionalized lignin-derived mesoporous carbon (LDM C-S O_3H)	-	261.7	0.067	3.42	100	98	[28]

4. CONCLUSIONS

A carbon-based solid acid catalyst was prepared from sugar bagasse. The catalyst featured an amorphous carbon structure with a high specific surface area (754.19 m^2/g) and a pore size distribution in the range of 2.5 - 2.9 nm. The total acid site density of the catalyst of 10.65 mmol/g was contributed by -OH, -COOH and -SO_3H groups. The contents of -COOH and -SO_3H groups were 34.83 % and 3.15 %, respectively.

The catalyst was applied to the dehydration of fructose into 5-HMF in DMSO solvent. The fructose was completely converted into 5-HMF with a selectivity of 93.22 % with the following reaction parameters: a catalyst loading of 5 wt.%, a reaction time of 2.5 h, and a reaction temperature of 100 °C.

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CrediT authorship contribution statement. Vu Nam Trung: Conceptualization, Methodology, Formal analysis, Writing – original draft. Vu Tue Minh: Conceptualization, Methodology, Formal analysis, Writing – original draft. Truong Duc Duc: Conceptualization, Writing – review & editing, Funding acquisition, Supervision. Le Quang Dien: Writing – review & editing, Supervision. Nguyen Trung Thanh: Writing – review & editing, Supervision. Tran Thi Thuy: Conceptualization, Writing – review & editing, Supervision.

Declaration of competing interest. The authors declare that they have no known competing financial interests or personal relationships that influence the work reported in this paper.

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