

# Preparation of Carbon-based Solid Acid Catalyst from Rice Straw for Furfural Production in Aqueous Media

Nhung Hong Nguyen,<sup>a,b,\*</sup> Son Anh Hoang,<sup>a</sup> Khanh Duy Pham,<sup>a</sup> and Trung Quoc Nguyen<sup>a</sup>

A powerful carbon-based solid acid catalyst and furfural were obtained from rice straw (RS) biomass resource. The acid catalyst was prepared through the carbonization and sulfonation of RS. Fourier transform infrared spectroscopy, energy-dispersive X-ray spectroscopy, scanning electron microscopy, N<sub>2</sub> adsorption-desorption, and ammonia temperature-programmed desorption (NH<sub>3</sub>-TPD) were used to characterize the catalysts. The effect of sulfonation time (4 h to 16 h) on the structure and acidity of the catalysts was elucidated. After 16 h of sulfonation, the BET surface area and the total acidity of the catalyst reached 415 m<sup>2</sup>/g and 7.48 mmol/g, respectively. Moreover, strong acid sites accounted for more than 63% of acidity. The catalyst was then used for the conversion of RS into furfural in water. The influence of reaction temperature and time while using the catalyst on the conversion process was also investigated. The catalyst exhibited high activity in the conversion of RS, with a furfural yield of 68.3 g/kg RS at 160 °C in 5 h.

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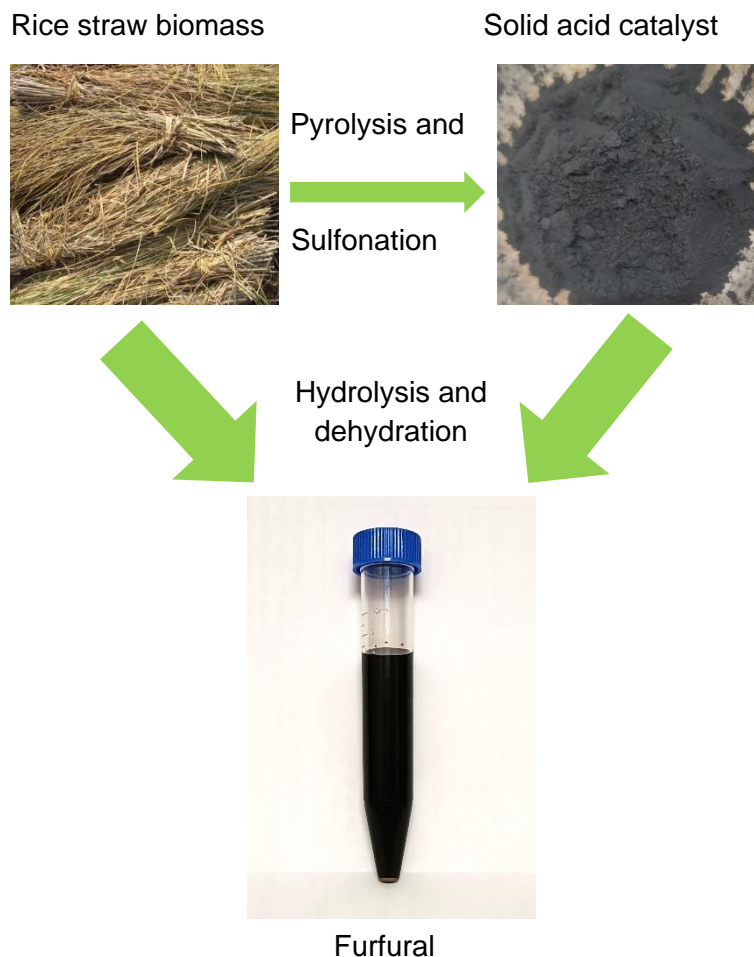
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Contact information: a: Institute of Materials Science, Vietnam Academy of Science and Technology, Hanoi 100000, Vietnam; b: Graduate University of Science and Technology, Vietnam Academy of Science and Technology, Hanoi 100000, Vietnam; \*Corresponding author: nhungnh@ims.vast.ac.vn

## INTRODUCTION

Furfural (FF) is a primary raw material in the chemical industry, from which many products, such as solvents, polymers, fuels, pharmaceuticals, agricultural products, and many other essential chemicals, can be synthesized. Moreover, furfural is evaluated as a renewable, non-fossil fuel (Lange *et al.* 2012; Luo *et al.* 2019). Because the world is looking for alternative energy sources to crude oil, the production and use of furfural would play a central role and continue to grow in the future. Furfural is mainly synthesized from hemicellulose present in raw biomass, especially lignocellulosic biomass (Mariscal *et al.* 2016). Inorganic acids, such as H<sub>2</sub>SO<sub>4</sub>, HCl, and H<sub>3</sub>PO<sub>4</sub>, are commonly utilized as catalysts in the furfural production process from biomass (Gürbüz *et al.* 2013). Yadav carried out a series of experiments aimed at determining the optimal conditions for the conversion of furfural from rice straw with the presence of phosphoric acid (Yadav *et al.* 2016). The optimal reaction conditions led to a furfural yield of 4.85 g/L, which were identified as a liquid-solid ratio of 6.0 (volume-mass), an acid concentration of 8% (w/v), a reaction temperature of 160 °C, and a reaction time of 150 min. Sherif employed a combination of simulation and experimentation in order to optimizing the furfural synthesis process from rice straw utilizing H<sub>2</sub>SO<sub>4</sub> as the catalyst. With an initial rice straw feed of 100 kg/h, and the volume of sulfuric acid of 12.78 L/h, following two reaction stages, which involve the initial reaction at 121 °C and the subsequent conversion of xylose to furfural at 200 °C, the

overall reaction results in the production of furfural at a yield of 12.9 kg/h (Sherif *et al.* 2021). However, the use of homogeneous acid catalysts in dehydrating hemicellulose to furfural causes many severe problems of environmental pollution and equipment corrosion (Liu *et al.* 2018). To solve these obstacles, solid acid catalysts have been increasingly considered as promising alternative catalysts to facilitate a cleaner, safer, and cheaper process for furfural production (Wang *et al.* 2020; Hoang and Cuong 2021).



**Fig. 1.** Furfural production from rice straw biomass

Solid acid catalysis made from carbohydrates was discovered for the first time using glucose as a raw material, consisting of two successive steps: partial carbonization of glucose (creating biochar), followed by sulfonation of the obtained biochar (Toda *et al.* 2005; Mo *et al.* 2008). The catalyst was shown to possess an acidity comparable to that of sulfuric acid, and stronger than those based on sulfated zirconium, amberlyst-15 resin, or niobic acid (Zong *et al.* 2007). The catalyst, also known as carbonization catalyst, was shown to have many advantages regarding acidic strength and structure. Structurally, the catalyst framework was formed by many condensed aromatic polycyclic systems, with C atoms possessing many hybridization states from  $sp$ ,  $sp^2$  to  $sp^3$ , so it could exist in many different types of structures such as layers, tubes, or spheres. Unlike carbon graphite in the crystalline state, the carbonization catalyst existed in the amorphous state. The highly porous 3D structure made it convenient for the functionalization process (Franklin 1951)

then the group with strong acid force (-SO<sub>3</sub>H) was successfully grafted through sulfonation. Zhang (2016) reported that sulfonated carbon was employed as a catalyst for converting xylose and corn stalk into furfural in  $\gamma$ -valerolactone with high yields of 78.5% and 60.6%, respectively. Xu *et al.* (2021) used a carbon-based solid acid prepared from pectin as the catalyst for converting xylose to furfural in a mixed solvent consisting of water and  $\gamma$ -valerolactone. A furfural yield of 80.4% and a xylose conversion of 100% were obtained at 170 °C for 60 min.

Rice straw contains about 39.5% cellulose, 24.5% hemicellulose, and 15.9% lignin as reported by Kim *et al.* (2011). Rice straw has more hemicellulose than some other plants such as softwood species (Van Hung *et al.* 2020). According to the International Rice Research Institute, Vietnam is the world's 5<sup>th</sup> largest rice exporter. Each year in Vietnam, more than 20 million tons of RS are burned, out of a total of about 50 million tons generated by agriculture (Pham *et al.* 2022). This has been a huge waste of resources and is very unfortunate. In addition, making freckles also pollutes the environment, emits greenhouse gases, and obstructs traffic. Many other international assessments also showed that Vietnam has open-ended biomass resources with great potential for reuse but has not been effectively applied.

In this study, rice straw was used as a source of biochar for catalytic preparation and as a raw material for furfural synthesis. The influence of sulfonation time on the structure and acidity of the prepared catalysts was revealed as well as the effect of biomass conversion reaction temperature and time on furfural yield was explored. These results show potential for the clean conversion of RS into bio-based chemicals.

## EXPERIMENTAL

### Materials

Rice straw (*Oryza sativa*) collected from the North of Vietnam was used to prepare the biomass feedstock. The 98% sulfuric acid and furfural (99%) were purchased from Sigma. Double-distilled water was prepared in the laboratory. The raw RS was dried at 100 °C to constant weight to eliminate all the free water. Then, the dried RS was cut and ground to 40-mesh size. After that, ground RS was washed with deionized water to remove dust. Finally, the RS was dried at 100 °C to a constant weight.

### Preparation of Catalyst

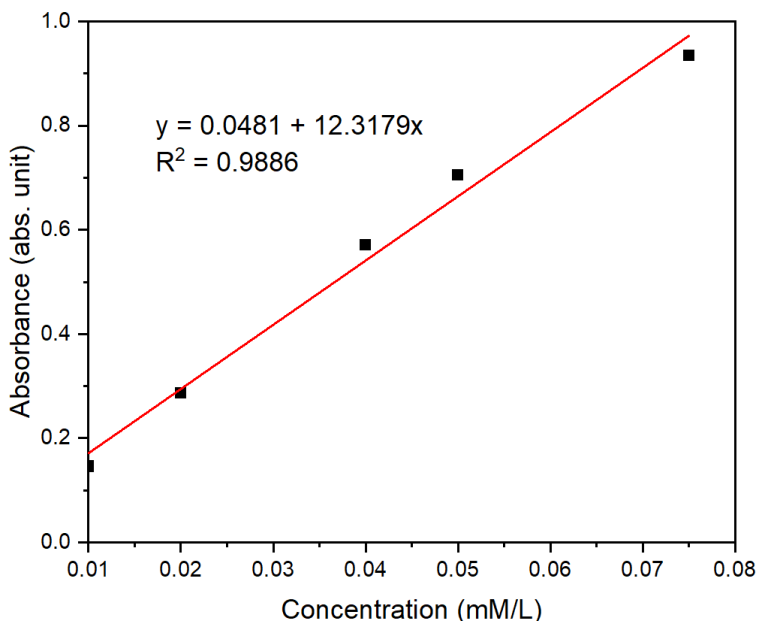
Biochar and sulfonated biochar catalysts were synthesized according to the methods described below. The dried RS (5 g) was partially carbonized at 300 °C in N<sub>2</sub> atmosphere for 2 h to produce biochar. Subsequently, the biochar was submerged once in ethanol and treated with ultrasonic cleaning for 30 minutes to eliminate the tar formed in the carbonization procedure then filtered and dried for 5 h at 80 °C. For the sulfonation process, 3 g of the prepared biochar (BC) was impregnated in the round-bottomed flasks with 10 mL of concentrated H<sub>2</sub>SO<sub>4</sub> and ultrasonicated at 150 °C for 4, 8, 12, and 16 h. The catalysts were denoted as SBC-X, where “X” is the sulfonation time. After all, the sulfonated biochar was separated by vacuum filtration, washed with hot distilled water to neutralize pH, and then dried at 100 °C overnight.

## Activity of CSAC Catalyst through the Synthesis of Furfural from Rice Straw Hydrolysate

The catalytic conversion of RS to furfural was performed in a high-pressure stainless-steel reactor equipped with a mechanic stirrer and electric-heating temperature controller. In one stage procedure, a mixture of rice straw (20 g), the SBC-16h catalyst (2.0 g), and distilled water (200 mL) was charged into the reactor, heated from room temperature to the desired temperature (150, 170, 190, and 200 °C), and allowed to react for different reaction time (1, 3, 5, and 7 h). After the reaction time, the product was collected by filtration and the furfural concentration in the filtrate was analyzed using UV-Vis spectroscopy.

### Characterizations

Many techniques were used for characterizing the catalyst, including Fourier transform infrared (FTIR), scanning electron microscopy (SEM), electronic dispersive X-ray photospectroscopy (EDX), N<sub>2</sub> adsorption-desorption analysis, and ammonia temperature-programmed desorption (NH<sub>3</sub>-TPD). The FTIR spectra were recorded on Nicolet 6700 FT-IR Spectrometer using KBr pellets over the range from 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup>. The SEM images and EDX spectroscopy were performed on a Hitachi S-4800 device. The N<sub>2</sub> adsorption-desorption analysis was measured by BET analysis using MicroActive for TriStar II Plus Version 2.03 at 77K; the degasification was established at 423 K for 3 h under high vacuum pressure. The acidity of the catalyst was determined by NH<sub>3</sub>-TPD using AutoChem II 2920. <sup>1</sup>H NMR spectra of received furfural after extraction and distillation were recorded on Bruke Biospin AvanceNEO 600 MHz in CDCl<sub>3</sub>.



**Fig. 2.** Calibration curve of furfural in double-distilled water at different concentrations

Because furfural has strong absorption in ultraviolet at a wavelength of 277 nm (Martinez *et al.* 2000), the furfural content in the hydrolysates was analyzed by ultraviolet-visible spectroscopy (UV-Vis). Before analysis with UV-Vis, the hydrolysates were distilled to eliminate the interference from acid-soluble lignin. The distillates were diluted

with double-distilled water to obtain absorbance values between 0.1 to 1.0. Then, the furfural concentrations of the distillates were calculated from the calibration curve of high-purity furfural (> 99%, Sigma-Aldrich). The calibration graph of furfural was attained from the absorption spectrum of a set of concentrations (from 0.01 to 0.75 mM/L) at 277 nm (Fig. 2). The UV-Vis spectra were obtained using Lambda 35 UV-Vis. Moreover, the yields of furfural on a dry weight basis of RS were calculated using the following Eq. 1,

$$\text{Furfural yield} = \frac{\text{mass of furfural formed (g)}}{\text{mass of RS (kg)}} \quad (1)$$

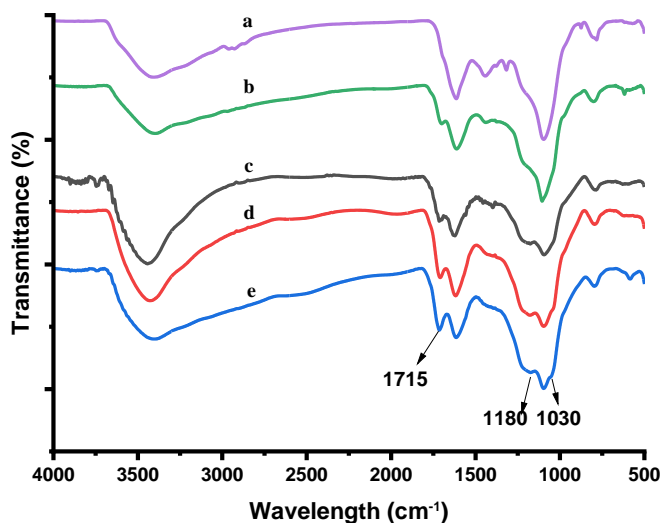
where the yields of furfural are expressed as g furfural/kg RS.

## RESULTS AND DISCUSSION

### Characterization of the Prepared Catalysts

#### FTIR analysis

Biochar (BC) is obtained from RS after pyrolysis, and it possesses a poly-condensed aromatic ring system. Followed by this partial carbonization process, the process of sulfonating the material to attach strong acid  $-\text{SO}_3\text{H}$  groups into the condensing polycyclic system was performed. Therefore, infrared spectroscopy (FTIR) is a valuable method to demonstrate the presence of important functional groups in the catalyst. Infrared spectra of biochar and the SBC catalyst are shown in Fig. 3.



**Fig. 3.** FT-IR spectra of the catalysts with different time of sulfonation

The FTIR spectra of BC (Fig. 3a) and SBC catalysts (Fig. 3b through 3e) showed the appearances of similar functional groups, *e.g.*  $-\text{OH}$ ,  $-\text{C}=\text{C}$ , and  $-\text{C}-\text{O}$  groups, at wavenumbers of  $\sim 3400 \text{ cm}^{-1}$ ,  $1607 \text{ cm}^{-1}$ , and  $1100 \text{ cm}^{-1}$ , respectively, which characterized the system of common functional groups in biochar (Wei *et al.* 2020). In the SBC catalyst, the new bands at 1030, 1180, and  $1705 \text{ cm}^{-1}$  were the peaks characteristic for the stretching mode of  $\text{O}=\text{S}=\text{O}$  bonds of  $-\text{SO}_3\text{H}$  group and the stretching vibration of  $-\text{C}=\text{O}$  bond (Ouyang *et al.* 2014; Tao *et al.* 2015). These bands were not present in the FT-IR diagram

of the BC sample, convincingly demonstrating that  $-\text{SO}_3\text{H}$ ,  $-\text{OH}$ , and  $-\text{COOH}$  groups were successfully introduced into the carbon framework of biochar (Xiong *et al.* 2018; Efiyanti *et al.* 2020; Zhou *et al.* 2021). It can be seen that when the time of sulfonation process was prolonged from 4 to 16 h, the intensity of these identical peaks also increased. It is known that  $-\text{SO}_3\text{H}$  groups in an alkaline medium will exist in the form of  $-\text{SO}_3^-$ , which, together with the hydrophobic radical of biochar, will be equivalent to an anionic surfactant. Thus, a material that was slightly soluble in water, such as biochar, has been transformed into a material that is highly soluble in water through the sulfonation process, thereby improving the efficiency of diffusion of the catalyst into the solution, which would be beneficial for the catalysis stage.

### SEM and EDX Analysis

The surface morphology and the EDX spectrum of the BC and the SBC-16h are shown in Fig. 4. The elemental analysis of the obtained sulfonated catalysts is summarized in Table 1. It could be seen that the porous structure of the synthesized catalysts in this study was the same as biochar reported from different carbon sources (Thanh *et al.* 2020; Ahmad *et al.* 2023). After the reaction with sulfuric acid, partial degradation of carbon structure and dissolution of the K, Ca, and Mg compounds made larger pores, but the surface morphology was still conserved. Large changes in elemental composition in the samples before and after sulfonation were observed.

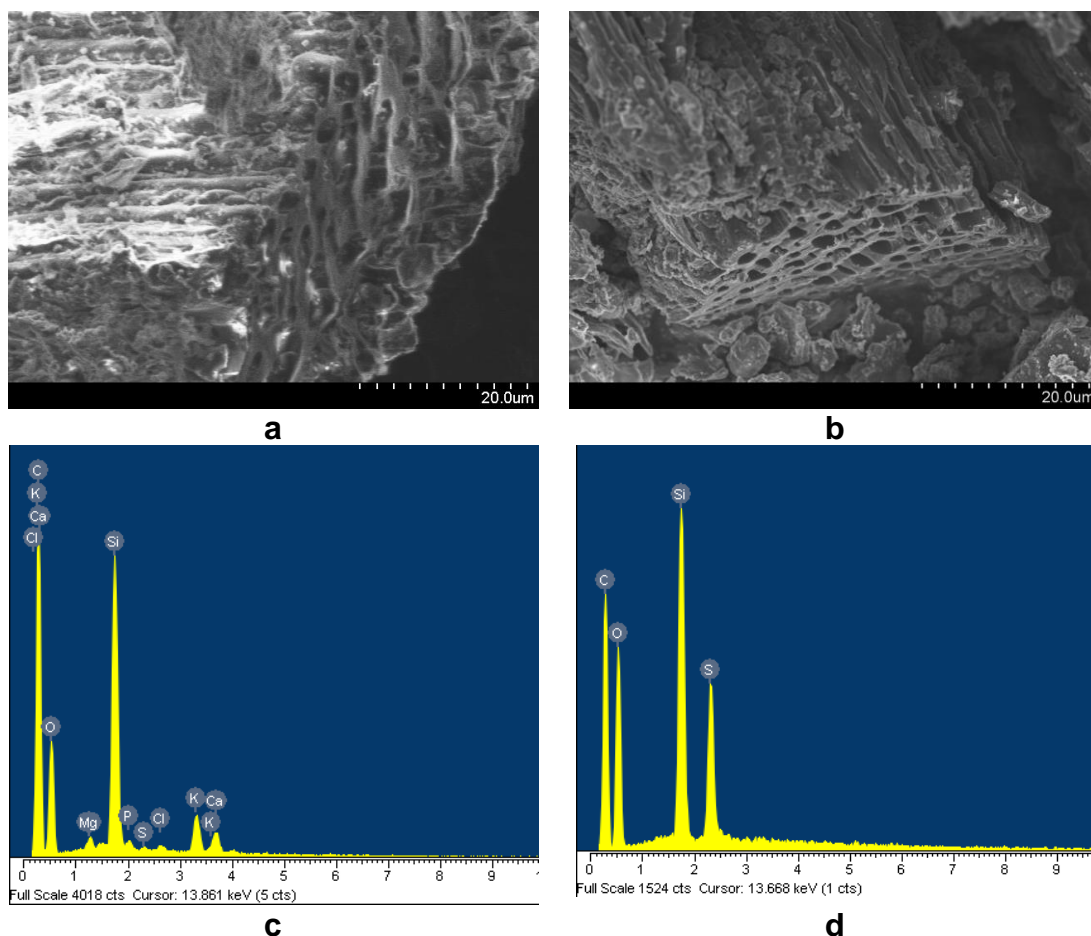


Fig. 4. SEM and EDX spectrum of the BC (a, c) and SBC-16h (b, d)

**Table 1.** Element Analysis by EDX of the Catalysts with Different Time of Sulfonation

Sample	C (%)	O (%)	Si (%)	S (%)	Others (%)
BC	63.70	27.05	6.52	0.09	2.63
SBC-4h	54.22	36.44	7.67	1.67	
SBC-8h	46.71	44.97	6.35	1.97	-
SBC-12h	51.85	39.85	5.62	2.49	-
SBC-16h	49.38	38.81	7.63	4.17	-

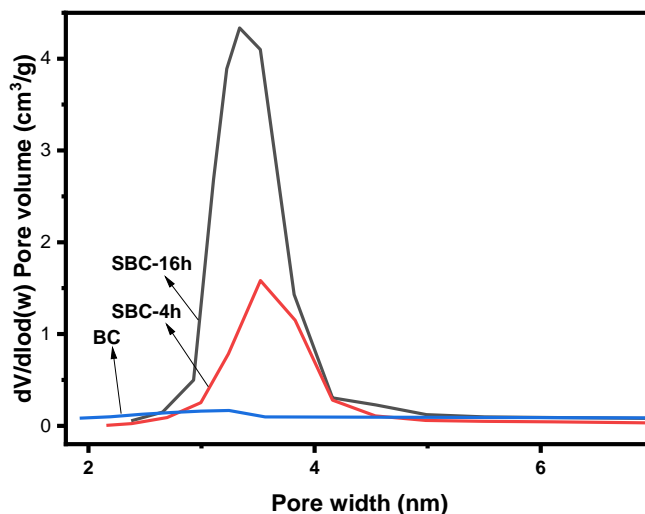
In addition to the main components of C, and O, the BC sample also had Si, K, Ca, Mg, and a small amount of S (0.09 wt%) contents. After the sulfonation process, alkaline and alkaline earth metal elements, such as K, Ca, and Mn, were no longer present. The sulfur content was much higher than that from biochar. The sulfur content also rose from 1.67 to 4.17 wt% as the sulfonation time increased. The S content of the SBC-16h reached 4.17 wt%, which was quite high in comparison with the results reported by Wei *et al.* (2020) and Xiong *et al.* (2018). This was also consistent with the nature of the sulfonation process, in which many -SO<sub>3</sub>H groups are introduced into the condensed aromatic polycyclic system of biochar. Thus, through the above FTIR and EDX analysis results, it could be seen that biochar and sulfonated biochar did not differ in basic structure frame, which mainly consisted of condensed aromatic polycyclic systems, a consequence of the incomplete carbonization of rice straw. The difference was in the amount of -SO<sub>3</sub>H group present in sulfonated biochar. The -SO<sub>3</sub>H group helps in increasing the acidity of biochar, transforming biochar from a material that was almost insoluble in water into a material that could be dispersed in water.

### N<sub>2</sub> Absorption – Desorption Analysis

The BET specific surface area, pore diameter, and pore volume of BC, SBC-4h, and SBC-16h are summarized in Table 2 and Fig. 5. The BET specific surface area of the BC sample reached 121 m<sup>2</sup>/g. While the BET surface area of SBC-16h was more than 3 times larger than BC, the pore diameter calculated by the BJH method of the SBC samples was slightly higher after sulfonation. In addition, the pore volume of the sulfonated samples exhibited an elevated numerical value. The pore volume of SBC-16 was also increased to 0.62 cm<sup>3</sup>/g in comparison with that of the BC sample. The results emphasized the effect of time on the sulfonation efficiency. At the same time, these results are consistent with the results from SEM images and EDX analyses. The increases in pore volume and BET surface area show that changes in structure had taken place after the sulfonating process, including collapse because of the dehydration by concentrated sulfuric acid and degradation of the carbon.

**Table 2.** Surface Area and Pore Parameters of the Prepared Catalysts

Sample	BET (m <sup>2</sup> /g)	Average Pore Diameter (nm)	Pore Volume (cm <sup>3</sup> /g)
BC	121	3.26	0.05
SBC-4h	167	4.24	0.21
SBC-16h	415	5.01	0.62



**Fig. 5.** Pore diameter distribution due to volume of the prepared catalysts

The structural changes may be a consequence of partial pore and surface cracking in BC by glycosidic bond breakage of cellulose and hemicellulose during the sulfonation process (Inagaki 2009).

### NH<sub>3</sub>-TPD Analysis

The acid sites of catalysts commonly are divided into three categories according to the differences in desorption temperature, 50 to 190 °C belonging to weak acid sites, 190 to 400 °C belonging to medium acid sites, and > 400 °C belonging to strong acid sites (Ding *et al.* 2018). The total acidity and the percentage of acid site (according to % of total acid) were calculated from NH<sub>3</sub>-TPD analysis of prepared SBC are presented in Table 3. The total acidity was considerably raised from about 0.6 to 7.48 mmol/g with a prolonged reaction. It is noteworthy that, with all samples, strong acid sites (> 400 °C) contributed to more than 50% of acid density. Compared with recent works, where the acidity of the obtained catalyst was less than 5.08 mmol/g (Thanh *et al.* 2020) or even 3.01 mmol/g (Esmaeili *et al.* 2023), this study achieved better results. In addition, these results were fully consistent with that of FTIR analysis as well as EDX. Therefore, it could be concluded that the acidity of SBC-16h was very high. In addition, with high BET and pore structure, the catalyst had a huge potential as a catalyst in many synthesis applications.

### Activity Study of the SBC Catalyst Through Furfural Synthesis from Rice Straw

#### *Effect of reaction temperature*

As discussed above, the synthesized SBC-16h sample had a very high total acid site density, especially strong sites. In addition, there were many -SO<sub>3</sub>H groups in the structure of the SBC so this catalyst could disperse well in water. Therefore, the as-prepared SBC could be used as a heterogeneous solid acid catalyst for the conversion of rice straw into furfural instead of homogeneous acids. To evaluate the catalytic activity and explore the optimum time and temperature for the reaction conversion, experiments were conducted with a weight ratio of RS to water of 1:10; and catalyst loading (to RS weight) of 10%. The temperature of the reactor was raised from room temperature to the determined temperature



(120 to 180 °C) and kept for a set time (1.0 to 7 h) allowing the hydrolysis and dehydration to occur.

**Table 3.** Total Acidity and Strength Distribution of SBC Catalysts with Various Sulfonation Time

Sample	Total Acidity (mmol/g)	Percentage of Acid Sites (%Total Acid)		
		Weak Acid (50 to 190 °C)	Medium Acid (190 to 400 °C)	Strong Acid (> 400 °C)
SBC-4h	0.60	10.93	38.41	50.66
SBC-12h	5.26	13.89	23.15	62.96
SBC-16h	7.48	14.99	21.10	63.91

The obtained furfural yields are summarized in Table 4 and Fig. 6. To investigate the effect of temperature, the reaction time was set for 3 h. The achieved results showed that when the reaction temperature was raised from 120 to 160 °C, the furfural yield was significantly increased from 24.30 to 51.91 g/kg. At low temperatures, the movement, the diffusion, and so the effective collision of the reagent molecules in the reaction solution were insufficient. Consequently, the reaction velocity and yield of the product were low. Raising temperature made these mentioned factors increase; hence the reaction velocity and furfural yield were elevated. When the temperature reached 160 °C, the obtained furfural yield was 51.9 g/kg. However, the productivity of furfural at 180 °C was slightly lower. There was a change in product color from brown to dark brown. The change in product color indicated the formation of by-products such as humins. These unwanted side-products were the result of condensation and polymerization of furan compounds at high temperatures (López *et al.* 2005; Li *et al.* 2018). Consequently, the reaction temperature was chosen at 160 °C for further study.

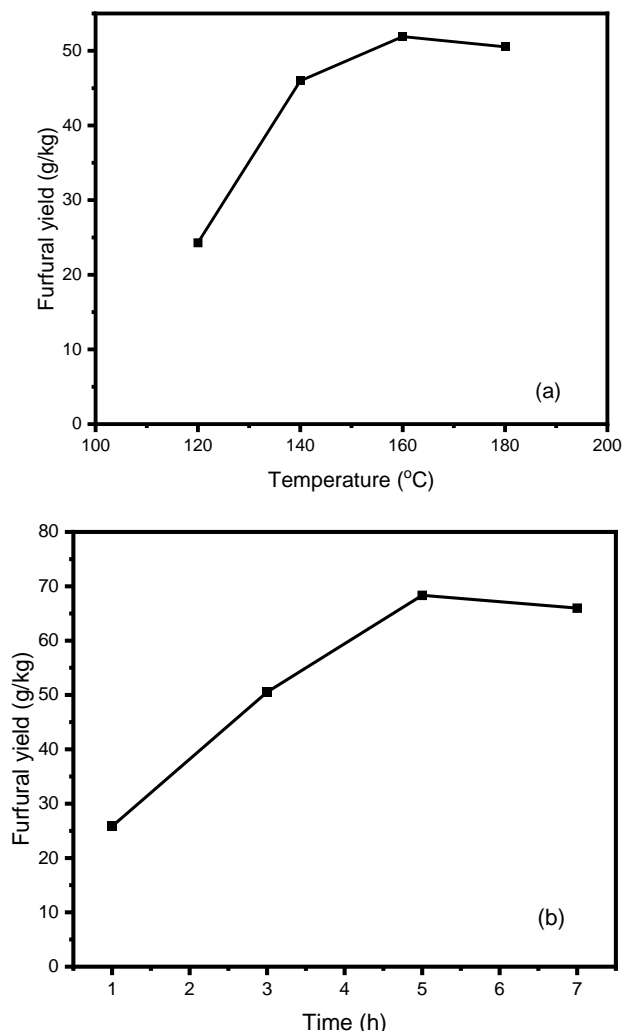
**Table 4.** Furfural Yield with Various Reaction Conditions

Entry	Reaction Temperature (°C)	Time (h)	Furfural Yield (g Furfural/kg RS)
1	120	3	24.3
2	140	3	46.0
3	160	3	51.9
4	180	3	50.5
5	160	1	25.8
6	160	3	51.9
7	160	5	68.3
8	160	7	66.0

#### *Effect of reaction time*

The influence of time on the furfural yield of RS conversion with the SBC-16h catalyst was examined. It can be seen in Fig. 6 that the furfural yield reached the highest value of 68.3 g/kg when the reaction time was 5 h. The amount of furfural in the product solution was considerably reduced with the prolongation of reaction time. The loss of furfural yield as mentioned above was considered to be because of condensation and polymerization of furan compounds. These results showed that the optimum time for RS conversion to furfural by the SBC-16h catalyst was 5 h. In comparison with the highest yield of 59 g/kg using H<sub>2</sub>SO<sub>4</sub> 0.5% as reported by Amiri *et al.* (2010), or 29.1 g/kg using 8% H<sub>3</sub>PO<sub>4</sub> reported by Yadav *et al.* (2016), the furfural yield from this study was higher.

The achievements of this work showed the high potential for the application and development of sulfonated carbon solid acid catalyst from RS as a heterogeneous catalyst for the conversion of furfural from RS in aqueous media.



**Fig. 6.** Furfural yield with various reaction temperature (a) and time (b) (Reaction conditions: (a) 20 g RS, 2 g SBC-16h, 200 mL distilled water, 3 h; (b) 20 g RS, 2 g SBC-16h, 200 mL distilled water, 160 °C)

## NMR Analysis

Upon completion of the reaction, the aliquot of the product was subjected to distillation and purification to facilitate the separation of the pure furfural. The structure of the received furfural was identified by  $^1\text{H}$  NMR spectrum (Fig. 7). It could be seen that the signal corresponding to the aldehyde proton was present at the typical high chemical shift value of  $\delta$  9.633 (1H). The proton signals from the ring were manifested as three distinct sets of signals within the chemical shift range of 6.57 to 7.67 ppm (3H) (Ismiyarto *et al.* 2017).

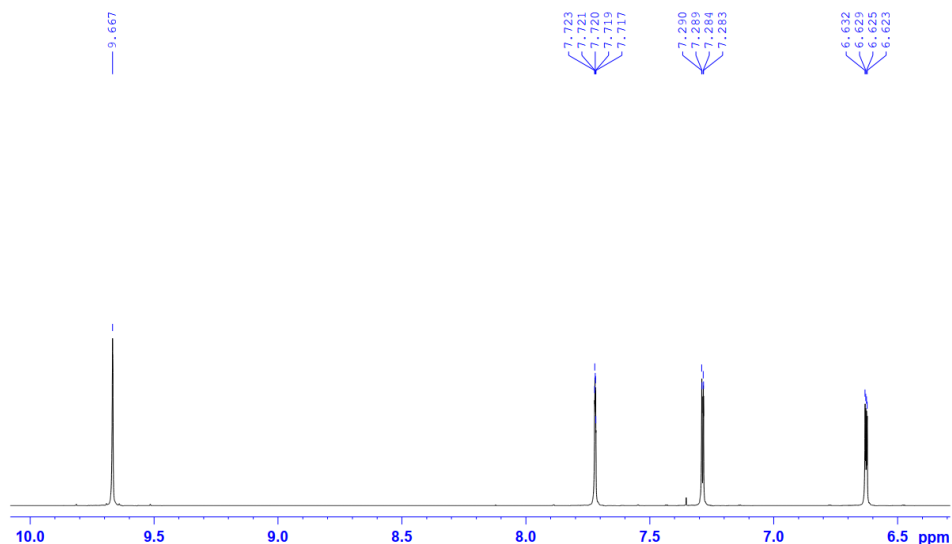


Fig. 7.  $^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ ) spectrum of furfural

## CONCLUSIONS

1. A highly active solid acid catalyst from rice straw (RS) biomass has been successfully synthesized by pyrolysis followed by sulfonation. The results of Fourier transform infrared (FTIR) and energy dispersive X-ray (EDX) analysis confirmed that the sulfonation process had introduced many  $-\text{SO}_3\text{H}$  groups bonded to the polyaromatic rings.
2. The effect of sulfonation time on the structure and acidity of the prepared catalyst was investigated. The optimum time for the sulfonating process of biochar at  $150\text{ }^\circ\text{C}$  was 16 h. The synthesized catalyst had a relatively high specific surface area of  $415\text{ m}^2/\text{g}$ , strong acid site density gain of  $4.78\text{ mmol/g}$ , and total acid site density gain of  $7.48\text{ mmol/g}$ .
3. The conversion of RS to furfural using the SBC-16h was carried out. The influence of reaction temperature and time on furfural yield was explored. The highest yield of furfural reached  $68.3\text{ g/kg}$  rice straw at temperature of  $160\text{ }^\circ\text{C}$  and time of 5 h. The structure of the received furfural was identified by  $^1\text{H NMR}$  spectrum. The utilization of RS in manufacturing catalysts and converting biomass into furfural was found to be an effective and environmentally friendly method of utilizing biomass, in line with the trend towards sustainable economic development. Moreover, these carbon-based acid catalysts exhibit potential for applications in biodiesel synthesis and various other hydration processes (Pan *et al.* 2022; Wei *et al.* 2020; Zhang *et al.* 2023).

## ACKNOWLEDGMENTS

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