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ORIGINAL ARTICLE

# Preparation of biochar catalyst with saccharide and lignocellulose residues of corncob degradation for corncob hydrolysis into furfural

**Qing-yan Liu**[1] · **Fang Yang**[1] · **Xiao-feng Sun**[1] · **Zhi-hua Liu**[1] · **Gang Li**[1]

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**Abstract** This paper presented a novel process for production of furfural by hydrothermal degradation of corncob over biochar catalyst, in which it was prepared with the recycling degradation solution and lignocellulosic solid residues. The biochar catalyst was papered by lignocellulose residues and concentrated saccharide solution, and then impregnated in 0.5 mol/L sulphuric acid at room temperature for 24 h assisted by the ultrasonic vibration. In the system of recycling, 8.8 % lignocellulose residues and 100 % concentrated saccharide solution from corncob hydrolysis have been recycled. Hydrolysis of corncob was carried out at 180 °C for duration of 170 min over the biochar catalyst. The experimental results have shown that the furfural yield of up to 37.75 % and overall corncob conversion rate of 62.00 % could be achieved under optimum operating conditions for the catalysts preparation and the corncob hydrolysis. It is believed that the acid density of 4.27 mmol/g of biochar catalyst makes the $SO_3H$ groups cleave β-1,4 glycosidic linkages effectively and hydrolyze the cellulose and hemicellulose to water-soluble sugars, as well as to facilitate dehydration of xylose to give the product of furfural.

**Keywords** Corncob · Biochar catalyst · Hydrothermal degradation · Furfural

## Introduction

Furfural is a valuable chemical precursor and chemical platform for manufacturing biofuels, fine chemicals, pharmaceuticals, resins, and organic solvent. Industrial furfural is most commonly derived from pentosan-rich lignocellulosic biomass (corncob, wood chips and shell of cotton seeds) with a global annual production of over 200,000 tonnes [1, 2].

Due to its low cost and ready availability, corncob has been widely used for the industrial furfural production through conventional technology of 2–10 wt% sulfuric acid catalyzed hydrolysis. However, this process has a low yield of approximately 5–10 %, and generates a large quantity acidic wastewater and solid residues [3]. Therefore, efforts have been devoted to developing new catalyst for effective decomposition of corncob biomass and the catalytic system using inorganic salts has shown promising results. Zhang and his coworkers [4] reported that xylan impregnated in 1-butyl-3-methylimidazolium chloride favor the production of furfural with a yield of 84.8 % at 170 °C using $AlCl_3$ as catalysts. In a separate study by Choudhary et al. [5] with xylose as raw material, a furfural yield of 39 % was achieved by using combined catalysts of Lewis acids ($CrCl_3$) and Brønsted acids (HCl), compared to 29 % using HCl alone.

In search for new catalysts to replace the industrially used mineral acid catalysts, solid superacid has attracted attention. Choudhary et al. [6] has conducted experimental studies on Sn-beta zeolite and Amberlyst-15 cocatalyst in dehydration of xylose and achieved moderate 9.5 % yield of furfural in a single pot at 110 °C. In other xylose dehydration experiments, catalysts $SO_4^{2-}/SnO_2$, $SO_4^{2-}/TiO_2$ and $SO_4^{2-}/ZrO_2$ exhibited superior catalytic activity with furfural production yield being 26.6, 16.8 and 9.3 %, respectively [7]. However, using inorganic salts or solid superacid ($SO_4^{2-}/M_XO_Y$) is still not economically feasible for

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✉ Gang Li
ligang@hebut.edu.cn

[1] Hebei Provincial Key Lab of Green Chemical Technology and High Efficient Energy Saving, School of Chemical Engineering and Technology, Hebei University of Technology, Tianjin 300130, China

producing furfural at an industrial scale, because of the additional costs for catalyst separation and recovery operations.

Sulfonated carbon-based catalyst has also been studied widely, and some research has suggested that the apparent activation energy for the cellulose hydrolysis using the carbon-based catalyst is estimated smaller than that of sulfuric acid based catalysts [8]. It is interesting to note that the carbon-based catalyst enhances hydrolysis of cellulose and hemicelluloses and promotes the dehydration of glucose and xylose to form 5-hydroxymethylfurfural (HMF) and furfural. Sulfonated naphthalene-derived carbon catalyst was examined for degradation of cassava waste, 12.1 % yield of HMF and 2 % yield of furfural were obtained [9]. It is also reported that a total sugar yield of 72.7 % was obtained from cellulose in ionic liquid 1-butyl-3-methylimidazolium chloride by applying sulfonated glucose-derived carbon catalyst [10].

The objective of the current study is to develop and test a new catalyst, biochar catalyst prepared from degradation solution and lignocellulosic solid residues of corncob, to produce furfural through corncob hydrolysis. In addition, an environmentally friendly system was developed by recycling of solid residues and waste solvent as illustrated in Fig. 1. This process combines the utilization of agricultural residue in chemical production and reuse of waste degradation solution and lignocelluloses in biochar catalyst preparation.

## Experimental

### Materials

Corncob was supplied from a local farm located in Hebei Province, China. The corncob was chopped into small pieces and dried at 60 °C under vacuum for 24 h, and then sieved through 20 and 80 meshes to collect particles sized between 0.9 and 0.2 mm for experiments. The mass fraction of hemicellulose, cellulose and lignin in corncob used in this work was 38, 35 and 20 %, respectively. The chemicals and organic solvents used in experiment were all of analytical grades and purchased from Tianjin Kermel Chemical Reagents Co. Ltd, China. Distilled water was used in the preparation of all solutions.

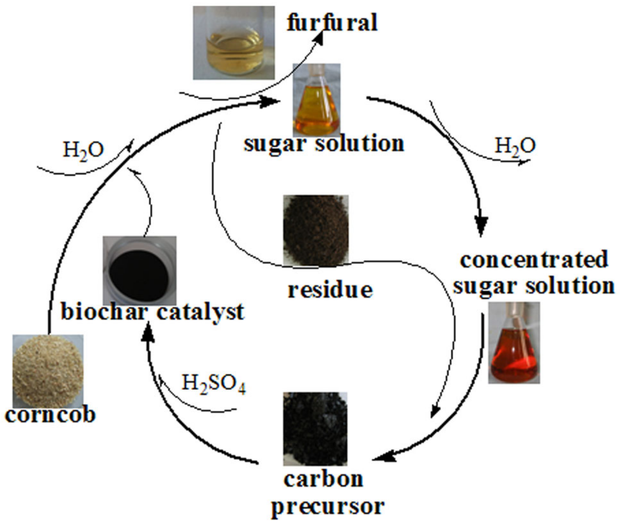

**Fig. 1** The recycling procedure of preparation of biochar catalyst and corncob degradation

### Preparation of biochar catalyst

1.5 g lignocellulose residue and 90 mL saccharide solution containing 20.70 g soluble reducing sugars were mixed and concentrated to paste by rotary evaporation at 45 °C under 0.090 MPa absolute pressure. The paste was then loaded into a high-pressure batch reactor made of stainless steel reactor with polytetrafluoroethylene liner. The paste was carbonized at a temperature of 180 °C with $N_2$ atmosphere for 48 h in a tube-carbide furnace. The carbonized solid mixture was ground into powder to be used as the carbon precursor material. According to the ratio of 1 g solid to 10 mL liquid, the carbon precursor material was impregnated in a pre-set concentration of sulphuric acid at room temperature for 24 h assisted by the ultrasonic vibration. The black solid obtained by centrifugation and drying at 80 °C for 12 h is finally ground into powder, ready as biochar catalyst.

### Characterization of biochar catalyst

Elemental analysis of the biochar catalysts mentioned above was conducted using a Flashea 1112 Series elemental analyzer to determine contents of C, H, N and S in samples. The acid density was measured by using Rick Ormsby's method [11]. The measurement of Brunauer–Emmer–Teller (BET) surface area, average pore width and pore volume were carried out by using Micromeritics ASAP 2020 Surface Area and Porosity Analyzer, in which the catalyst was pretreated initially at 80 °C for 4 h to remove any adsorbed species on the surface. The chemical structures were analyzed by FT-IR using a Nicolet MAGNA-560 spectrometer with KBr pressed pellet method. The morphology of the samples was examined by scanning electron microscopy (HITACHI S-4800 SEM). Powder X-ray diffraction (XRD) measurements of the carbon precursor and biochar catalyst were performed on a Rigaku D/max-2000 X-ray powder diffractometer with a Cu Kα radiation (40 kV, 40 mA) scanned over the $2\theta$ range of 10–80° steps of 4° with a count time of 1 min at each point. Thermogravimetric analysis was performed on a Perkin-Elmer 7 series thermal analysis system. About 10 mg of each sample were heated from 25 to 900 °C with a heating rate of 10 °C/min in $N_2$ gas at a flow rate of 50 $cm^3$/min (purity 99.998 vol%). $^{13}C$ MAS NMR spectra were measured at room temperature using a Bruker ASX-200 spectrometer at a Larmor frequency of 50.3 MHz. The bimodal Raman spectrum (Advantage NIR) of the catalyst was used to characterize its disordered carbon structure.

### Catalytic degradation of corncob

The catalytic degradation of corncob was performed in a stainless steel batch autoclave (CJF-0.25) equipped with a liner of polytetrafluoroethylene. Before each run, 5 g corncob, 0.3–0.5 g biochar-based catalyst and 40–100 mL water were charged in the reactor, and the mixture was then heated at 180 °C for 170 min in the oven. After the hydrolysis reactions, the mixture of corncob degradation solution and unreacted solid residue was separated by filtration. In this study, the effect of biochar catalysts made under different conditions on the corncob hydrolysis to furfural was investigated.

### Recycling utilization procedure of lignocellulose residue and concentrated saccharide solution

After the corncob degradation process, the lignocellulose residue was separated by filtration, and the concentrated saccharide solution was prepared by distilling the minimum-boiling azeotrope of furfural and water in the corncob degradation liquor at 45 °C under 0.090 MPa absolute pressure. They were re-used in the next run in preparation of carbon precursor material. Meanwhile with the purpose to increase the yield of furfural, the optimum preparation condition of biochar catalyst such as the ratio of lignocellulose residue to concentrated saccharide solution, carbonization temperature, impregnated concentration of sulfuric acid have also been investigated in this paper.

### Product analysis of furfural and sugars

Furfural in the degradation products of corncob was determined quantitatively by using HPLC instrument (Shimadzu, LC-20AD) equipped with a UV detector (Shimadzu, SPD-M20AV) and an Intersil ODS-EP C18 reversed-phase column (4.6 × 250 mm) at 40 °C column temperature. In the measurement, water and methanol (77:23, v/v) were used as the mobile phase with a flow rate of 1.0 mL/min and injecting sample solution of 20 μL in volume.

The total reducing sugar was measured using 3,5-dinitrosalicylic acid (DNS) method following procedures previously reported in the literature [12]. The analysis of compositions in the reducing sugar was performed by using HPLC (Alltech LC-2000ES) equipped with an ELSD detector and a XBridge BEH Amide Column (4.6 mm× 250 mm). The subsequent qualitative and quantitative analysis was carried out according to the method proposed by Guo et al. [13]. The pre-set chromatographic conditions are listed in Table 1.

### Determination of product yield and corncob conversion

The yields of furfural and soluble sugar, and the corncob conversion ratio were calculated based on the following equations.

$$\text{Furfural yield }\% = \frac{[\text{Furfural}]_{\text{mass}}}{[\text{Hemicellulose}]_{\text{massfraction}} \times [\text{Total corncob}]_{\text{mass}}} \times 100\ \%$$

$$\text{Soluble sugar yield }\% = \frac{[\text{Soluble sugar}]_{\text{mass}}}{[\text{Hemicellulose} + \text{Cellusose}]_{\text{massfraction}} \times [\text{Total corncob}]_{\text{mass}}} \times 100\ \%$$

$$\text{Corncob conversion yield }\% = \frac{[\text{Reacted corncob}]_{\text{mass}}}{[\text{Total corncob}]_{\text{mass}}} \times 100\ \%$$

## Results and discussion

### Optimized conditions for preparing biochar catalyst and corncob degradation

In the early stage of the experimental studies, corncob powder was degraded by hot compressed water in autoclave at 180 °C, with a mass–volume ratio of 1:10, the total reducing sugar yield of 50.3 % was obtained at 160 min.

**Table 1** The pre-set chromatographic conditions of gradient elution and ELSD detector

| Elapsed time (min) | Gradient solvent | | Drift tube temperature (°C) | Gas flow (L/min) | Impactor | Gain |
|---|---|---|---|---|---|---|
| | Acetonitrile % | $H_2O$ % | | | | |
| 0–60 | 85–50 | 15–50 | 95 | 2.0 | Off | 1 |
| 60–70 | 50 | 50 | | | | |

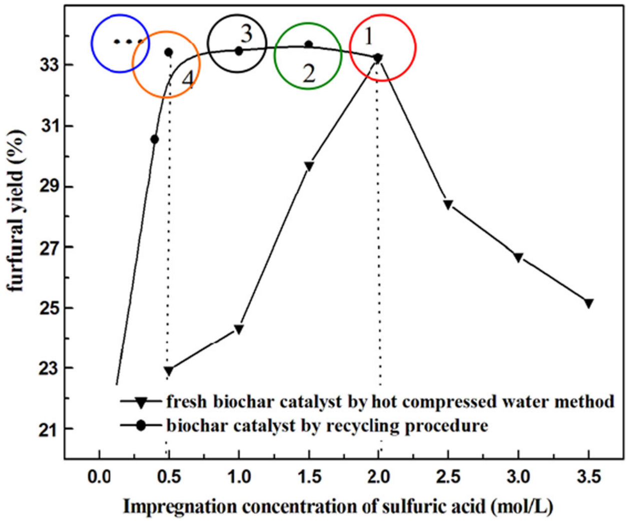

**Fig. 2** Effect of sulfuric acid impregnation concentration on the furfural yield. Biochar catalyst by recycling procedure was made in the typical way. In the corncob hydrolysis process, corncob (5 g), catalyst (0.4 g), and water (100 mL) were put into the autoclave, and the reactions were conducted at 180 °C for 170 min

The concentrated saccharide solution (pH = 4.5) and lignocellulose residue were employed to prepare carbon precursor in the typical way, and subsequently impregnated by pre-set concentration from 3.5 to 0.5 mol/L of sulfuric acid to make the initial biochar catalyst.

In the catalyst preparation and recycling application, the fresh biochar catalyst with impregnation concentration of sulfuric acid was varied from 0.5 to 3.5 mol/L, but the recycling biochar catalyst with impregnation concentration of sulfuric acid was limited from 0.1 to 2.0 mol/L. The effect of impregnation concentration of sulfuric acid on the furfural yield was summarized in Fig. 2. It can be seen that the catalytic action of fresh biochar catalyst with the impregnation concentration of sulfuric acid of 2.0 mol/L was best and the highest yield of furfural reached 33.29 %. When the biochar catalyst was turn into recycling procedure, it was found that the yield of furfural decreased from 33.29 to 21.47 % as the recycling biochar catalyst impregnated sulfuric acid from 0.5 to 0.1 mol/L. Therefore, the most suitable impregnated concentration of sulfuric acid for the recycling biochar catalyst was 0.5 mol/L and the pH value of the concentrated saccharide solution basically remained about 2.0 after the fourth cycle.

The preparation condition of catalysts with different mass–volume ratios of lignocellulose residues and concentrated saccharide solution and the carbonization temperature were examined in Table 2. From the results of furfural yield, it can be seen that the ratio of lignocellulose residue and concentrated saccharide solution is crucial to the catalytic performance (Runs 1–3), and the highest furfural yield of 33.29 % was achieved using catalyst made at 1.5 g:90 mL of lignocellulose residue to concentrated saccharide solution. By contrast, if the catalysts were prepared separately either using lignocellulose residues or concentrated saccharide solution or glucose for the corncob hydrolysis, as seen from Runs 6–8 in Table 2, the yields of furfural were lower than that of biochar-based catalysts as shown in Runs 1–3. The experimental results in Runs 2 and 4–5 indicated that 180 °C was an appropriate carbonization temperature for the preparation of carbon precursor material. In addition, the results of corncob hydrolysis by 0.8 wt% sulfuric acid and without any other catalysts are also listed in Table 2 as Runs 9 and 10 which gave the lowest furfural yields of 19.41 and 17.09 %, respectively.

**Table 2** Hydrolysis of corncob using biochar catalysts prepared in different ways

| Run | Catalyst[a] | Elemental content (%) | | | | Morphological properties | | Acid density (mmol/g) | Furfural yield (%) |
|---|---|---|---|---|---|---|---|---|---|
| | | C | H | O | S | $S_{\mathrm{BET}}$ ($m^2$/g) | $V_{\mathrm{total}}$ ($\times 10^{-3}$ $cm^3$/g) | | |
| 1 | A1.5 g-B120 mL-T180 °C | 63.77 | 4.19 | 24.94 | 6.10 | 4.92 | 4.23 | 3.89 | 30.41 |
| 2 | A1.5 g-B90 mL-T180 °C | 65.28 | 4.05 | 23.28 | 6.39 | 5.28 | 5.36 | 4.27 | 33.29 |
| 3 | A1.5 g-B60 mL-T180 °C | 66.98 | 3.98 | 21.22 | 6.82 | 8.71 | 9.84 | 4.77 | 29.91 |
| 4 | A1.5 g-B90 mL-T280 °C | 70.25 | 3.52 | 21.05 | 4.18 | 18.73 | 29.62 | 2.57 | 22.81 |
| 5 | A1.5 g-B90 mL-T380 °C | 73.57 | 3.21 | 19.09 | 3.13 | 23.42 | 37.21 | 2.18 | 20.49 |
| 6 | A10 g-T180 °C | 63.48 | 4.37 | 26.94 | 4.21 | 16.53 | 25.32 | 2.23 | 21.47 |
| 7 | B100 mL-T180 °C | 53.23 | 5.21 | 35.19 | 5.37 | 1.68 | 0.96 | 3.29 | 24.12 |
| 8[b] | Glucose100 mL-T180 °C | 52.61 | 5.36 | 35.60 | 5.43 | 1.26 | 0.75 | 3.36 | 27.86 |
| 9[c] | 0.8 wt% $H_2SO_4$ | – | – | – | – | – | – | – | 19.41 |
| 10 | None catalyst | – | – | – | – | – | – | – | 17.09 |

[a] A, B and T represent solid lingocellulose residues, concentrated saccharide solution and carbonization temperature in making the catalysts

[b] The feedstock in the preparing of biochar catalysts was glucose saturated solution

[c] The equivalent concentration of sulphuric acid was determined with the acid density 4.27 mmol/g of biochar catalyst. Reaction condition: 5.0 g corncob, 0.4 g catalyst, 100 mL water at 180 °C for 170 min

**Table 3** Effect of mass–volume ratio of corncob and water and catalyst dosage on the conversion ratio of corncob to furfural

| Mass–volume ratio of corncob (5 g) and water (mL) | Catalyst dosage (g)[a] | Conversion ratio (%) | Furfural yield (%) |
|---|---|---|---|
| 1:8 | 0.2 | 57.09 | 31.74 |
| | 0.3 | 56.32 | 29.13 |
| | 0.4 | 54.43 | 28.03 |
| 1:12 | 0.2 | 57.17 | 33.14 |
| | 0.3 | 62.00 | 37.75 |
| | 0.4 | 54.20 | 31.83 |
| 1:20 | 0.2 | 50.46 | 28.82 |
| | 0.3 | 53.63 | 31.54 |
| | 0.4 | 58.47 | 33.64 |

[a] The biochar catalysts were made at optimum conditions, and the hydrolysis solution and solid residues were recycled for four times. The reactions in the corncob hydrolysis process were conducted at 180 °C for 170 min

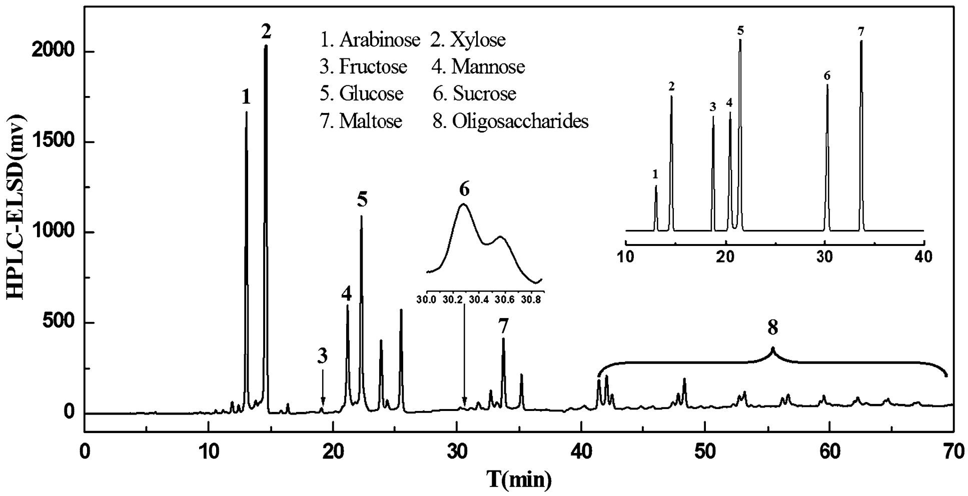

**Fig. 3** HPLC-ELSD chromatograms of water-soluble sugars in concentrated saccharide solution. The *chromatograms* of standard sugars mixture are also shown to compare the retention time

We also examined conditions in the corncob hydrolysis catalyzed by biochar catalysts made in optimized way, and the results are listed in Table 3. The suitable conditions for the production of furfural was as follows, 0.06:1 (w/w) of catalyst to corncob, 1:12 (w/v) of corncob to water, at a reaction temperature of 180 °C for 170 min, and the maximum yield of furfural can be 37.75 %.

The optimum number of biochar catalyst recycling is four. In the preparation process of biochar catalyst, 8.8 % lignocellulose residue and all of the concentrated saccharide solution were employed as raw material to prepare the catalyst precursor. The advantage of this procedure is to give full consideration of the waste material cycles and application as possible.

## Characterization of concentrated saccharide solution and lignocellulose residues

Lignocellulose can be hydrolyzed under acid conditions and produce arabinose, xylose, glucose and other compounds [14]. In the concentrated degradation solution of corncob hydrolysis, seven sugar components were identified as shown in Fig. 3 and the corresponding contents of these compounds are arabinose (5.53 %), xylose (9.96 %), fructose (0.63 %), mannose (2.50 %), glucose (0.11 %), sucrose (<0.01 %) and oligosaccharides (42.81 %) at optimum conditions, which the degradation solution was concentrated by distilling the minimum-boiling azeotrope of furfural and water at 45 °C under 0.090 Mpa absolute to 10 mL as the test sample. It was found that the yield of total reducing sugars was up to 63.01 % and most of oligosaccharides based, but the concentrated saccharide solution was not suitable for fermentation as the existence of HMF and acetic acid derived from the corncob degradation [15]. In future research, we will focus on transforming oligosaccharides to monosaccharide and further improving the furfural yield.

In this work, the conversion ratio of corncob during the degradation process was 84.93 %, mainly due to the saccharification of hemicellulose and cellulose as described in the literature [3, 9, 16]. From FT-IR spectra of corncobs before and after degradation as shown in Fig. 4,

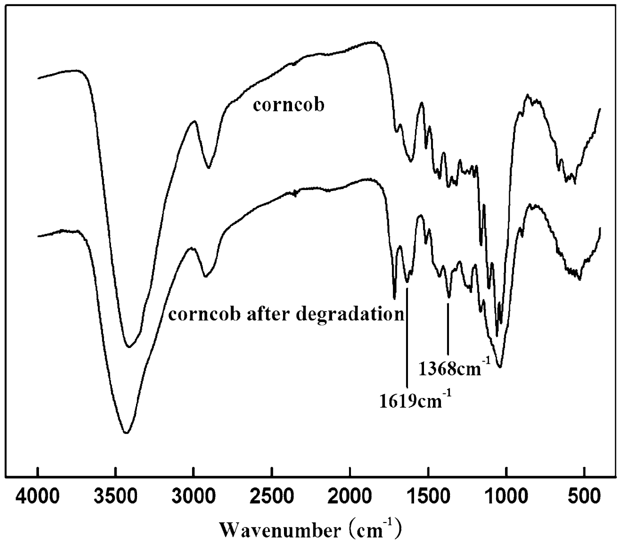

**Fig. 4** FT-IR spectra of corncob before and after degradation

lignocellulose residue of corncobs after degradation presents a stronger band at 1619 cm$^{-1}$ and other at 1368 cm$^{-1}$ due to C=C stretching in benzene ring [17]. Therefore, lignin, a natural polymer of methoxylated phenylpropane units [18], together with the partly unreacted cellulose account for the main composition of lignocellulose residue.

Biochar materials can be prepared by pyrolysis of carbonaceous materials which are rich in aromatic compounds such as naphthalene [9, 19], coconut shells [20], lignin [21], wood chips and peanut hulls [11], or other materials rich in pyranose ring such as starch [22], glucose [10], synanthrin [23] and cellulose [8]. In this work, carbon precursor was prepared by mixed materials with aromatic and pyranose ring structures as shown in Fig. 5.

Aromatic structure in lignocellulose residues plays an important role as the backbone chain to enhance the hardness of biochar material. In this way, a large proportion of pyranose ring in concentrated saccharide solution can transform into benzene ring during the carbonization process to enhance the stability of carbon precursor material [10]. The carbonization process may include reactions of glycosidation [24], caramelization [25] and aromatization [26]. The biochar catalyst was produced by the subsequent sulphonation at room temperature assisted by the ultrasonic vibration.

## Characterization of the biochar catalyst

Figure 6 shows the SEM images of carbon precursor and biochar-based catalysts. From the figure it can be seen that the morphology of target carbon precursor III shows irregular microspheres [27] with diameters 1–10 µm while the corresponding catalysts particles VI are more regular and apparently show lower viscosity after sulfuric acid impregnation. Comparison of the SEM images in combination with the experimental data from Runs 6–8 in Table 2 indicates that the interactions between sulfuric acid and sugary precursor are more intense than that between the sulfuric acid and sugarless ones, thus sugary catalyst has much higher sulphur content and acid density. However, the acid density of biochar catalysts decreased with increasing sugar content, falling from 4.77 mmol/g in Run 3 to 3.89 mmol/g in Run 1 due to the accompanying decrease of BET surface area and pore volume in carbon precursor.

From images of II and V, it is expected that the interactions of sulfuric acid on carbon precursor derived from concentrated saccharide solution alone are very strong so that it has obvious coking phenomena on the surface of SEM image V, which is not desired for catalysts. Adding lignocellulose residues to concentrated saccharide solution can prevent those phenomena to some extent; therefore, its biochar catalyst employed in catalytic degradation of corncob gave the highest furfural yield of 33.29 % in Run 2. Catalyst made in this way performed better catalytic activity than that prepared by lignin alone as tested in Run 6 or prepared by sugar alone as in Run 7.

The weight loss was measured when the carbon precursor and biochar-based catalysts were heated from 25 to 400 °C and the results are shown in Fig. 7a for the carbon precursor and in Fig. 7b for the biochar-based catalyst. It is found that the carbon precursor lost 22 % weight, whereas

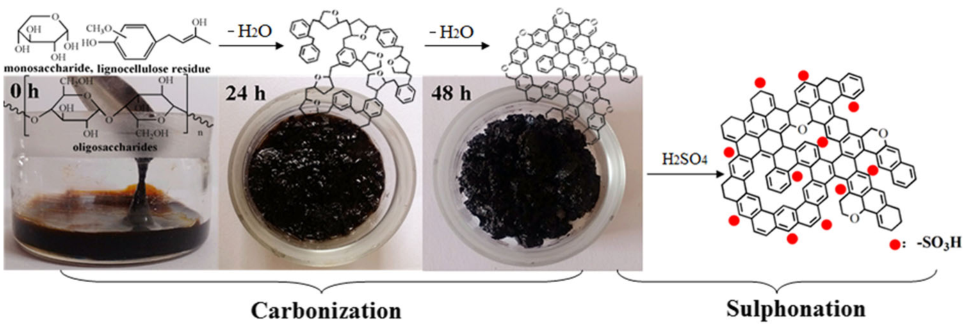

**Fig. 5** Images and supposed structure of the mixture of concentrated saccharide solution and lignocellulose residue after carbonization at 180 °C for 0, 24 and 48 h followed by sulphonation at room temperature for 24 h

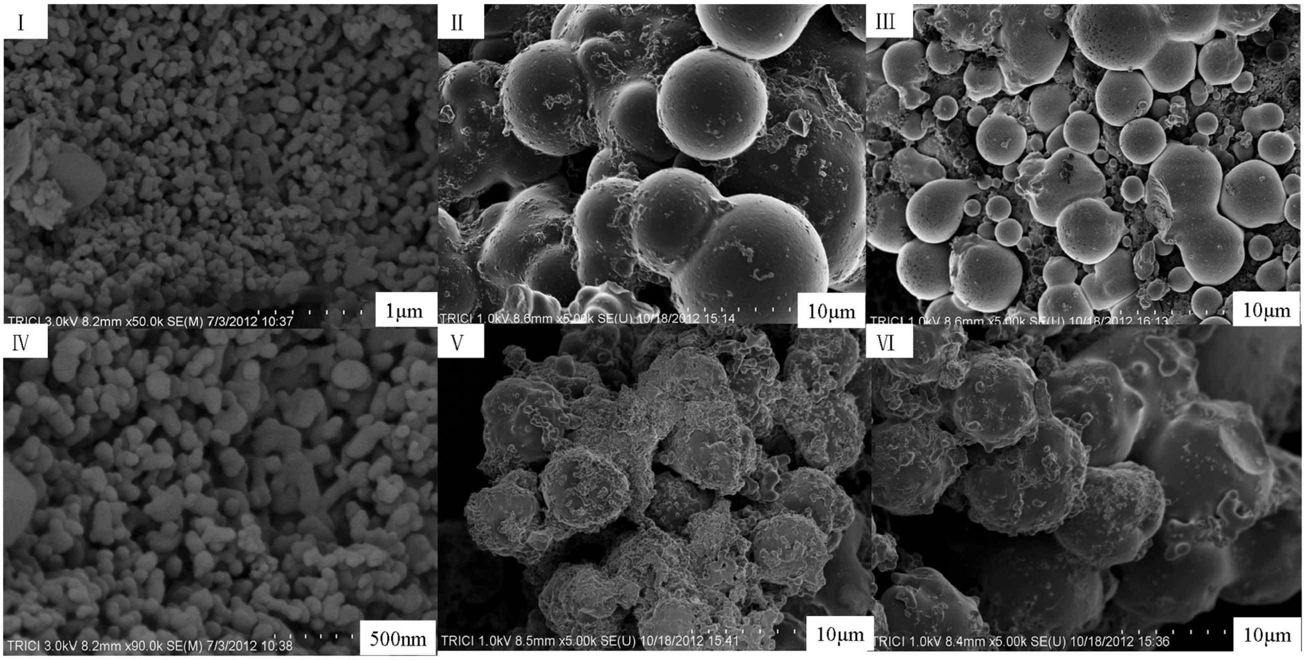

**Fig. 6** SEM images of carbon precursor and biochar catalyst. In the figure, I, II, III represent carbon precursor derived, respectively, from lignocellulose residue, concentrated saccharide solution and the mixture of these two materials at the concentration of lignocelluloses residues to saccharide solution of 1.5 g:90 mL. IV, V, VI represent the corresponding biochar catalyst from I, II, III impregnated in 0.5 mol/L sulphuric acid (1 g/10 mL) at room temperature for 24 h with the assistance of ultrasonic vibration

the biochar catalyst lost only 4 %. This clearly shows that the chemical structure of the biochar became more stable after carbon precursor material impregnated in sulphuric acid [8]. Therefore, the biochar catalyst is more suitable for the hydrolysis degradation of corncobs at a temperature of 180 °C.

Figure 8 shows the FT-IR spectra for carbon precursor (Fig. 8a) and biochar catalyst by Fig. 8b. From FT-IR spectra Fig. 8a, it is found that the absorption bands at 3422 $cm^{-1}$ can be assigned to OH bending vibration. Peak at 2910 $cm^{-1}$ is the characteristic of C–H stretching vibration of substituted alkyl groups. The absorption bands at 1716 and 1617 $cm^{-1}$ can be ascribed to $COO^-$ and C=C stretching vibrations, respectively [28]. Bands assigned to OH, COOH and C=C derived from lignocellulose residue and saccharide compounds.

In contrast, Fig. 8a, b shows three new bands at 870, 1068 and 1178 $cm^{-1}$ that could be assigned to the S–O–S stretching vibration, O=S=O asymmetric and symmetric stretching vibration in $SO_3H$ groups [29, 30]. The intensity of C–H band was decreased as the aromatization. All of the hydrophilic groups can promote the formation of carbon microspheres which is desirable for the biochar catalyst to be applied in aqueous solution with dispersion and stability [31].

The chemical shifts at 130, 155, and 180 ppm as shown in Fig. 9 are attributable to polycyclic aromatic carbon atoms, phenolic OH and COOH groups, respectively [10].

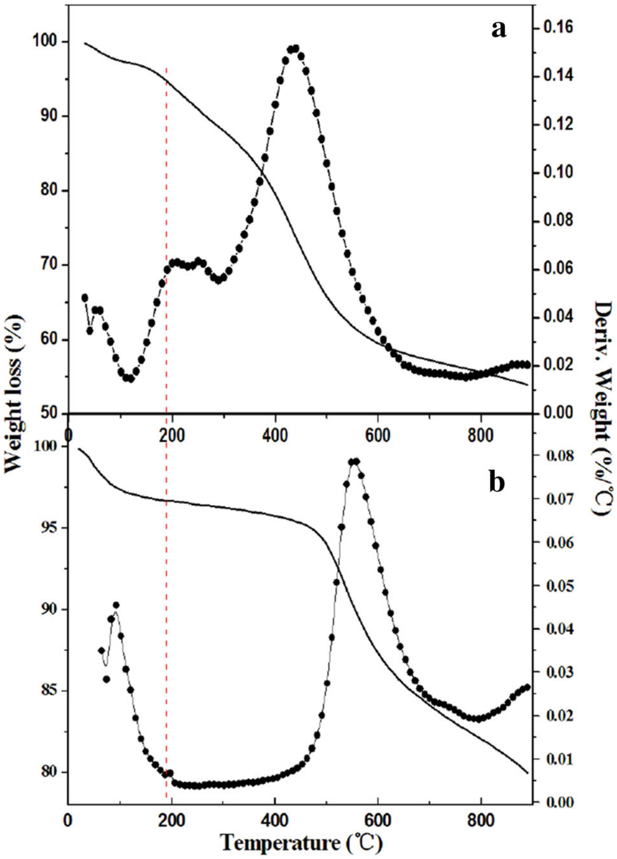

**Fig. 7** TG-DTG curves for **a** carbon precursor and **b** biochar catalyst

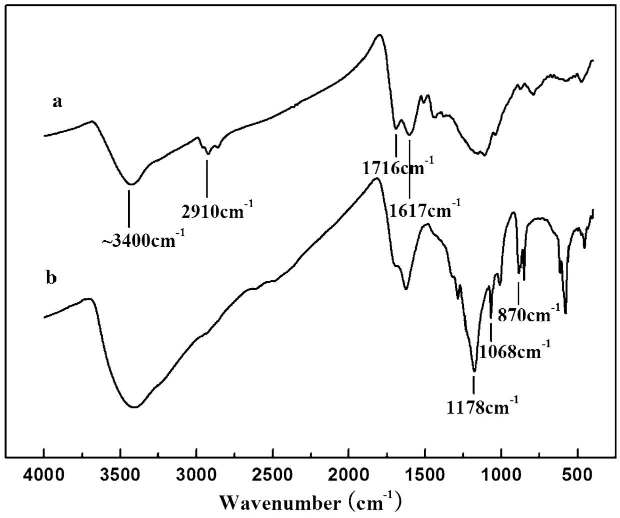

**Fig. 8** FT-IR spectra of **a** carbon precursor and **b** biochar catalyst

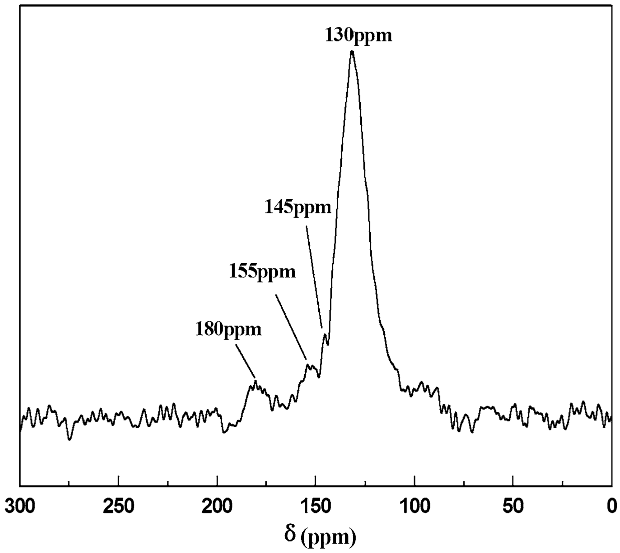

**Fig. 9** $^{13}$C MAS NMR spectrum of biochar catalyst

Although the main peak due to aromatic carbon connected with $SO_3H$ groups (Ar-$SO_3H$, ca. 140 ppm) is covered by the character of aromatic carbon atoms (130 ppm) and OH groups (155 ppm), the resonance shift at 145 ppm derived from Ar-$SO_3H$ is still visible.

The XRD patterns for the carbon precursor and biochar catalyst are shown in Fig. 10. From these XRD curves, two broad but weak diffraction peaks are observed at $2\theta$ angles of 10°–30° and 35°–50°, which indicate that both the carbon precursor and biochar catalyst are composed of aromatic carbon sheets oriented in a random fashion [32]. Peak at 35°–50° in Fig. 10b becomes more pronounced because of the sulphonation.

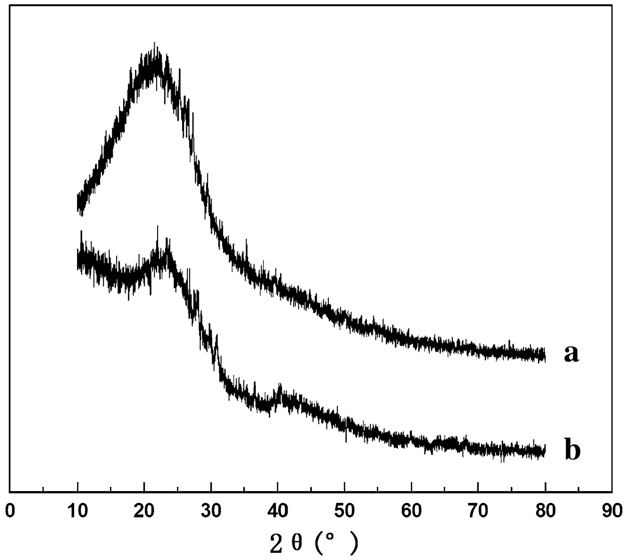

**Fig. 10** XRD pattern of **a** carbon precursor and **b** biochar catalyst

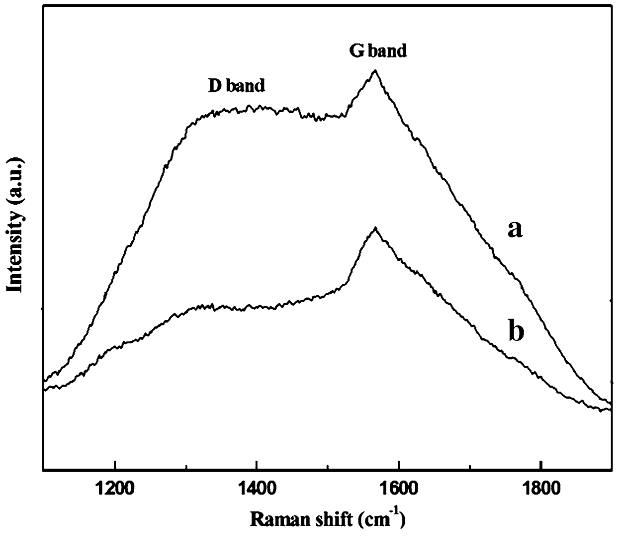

**Fig. 11** Raman spectra of **a** carbon precursor and **b** biochar catalyst

The Raman spectra in Fig. 11 display two broad signals assigned to the D band (1350 cm$^{-1}$, $A_{1g}$ D breathing mode, representative disordered structure) and G band (1580 cm$^{-1}$, $E_{2g}$ G mode, representative graphite structure). The intensity ratio of the D- to G-bands in Fig. 11a is smaller than that of in Fig. 11b. It indicates that biochar catalyst has a much higher degree of graphitization than carbon precursor [33].

## Suggested mechanism for corncob degradation over biochar catalyst

The degradation mechanism for corncob hydrolysis over biochar-based catalyst to produce furfural is proposed as

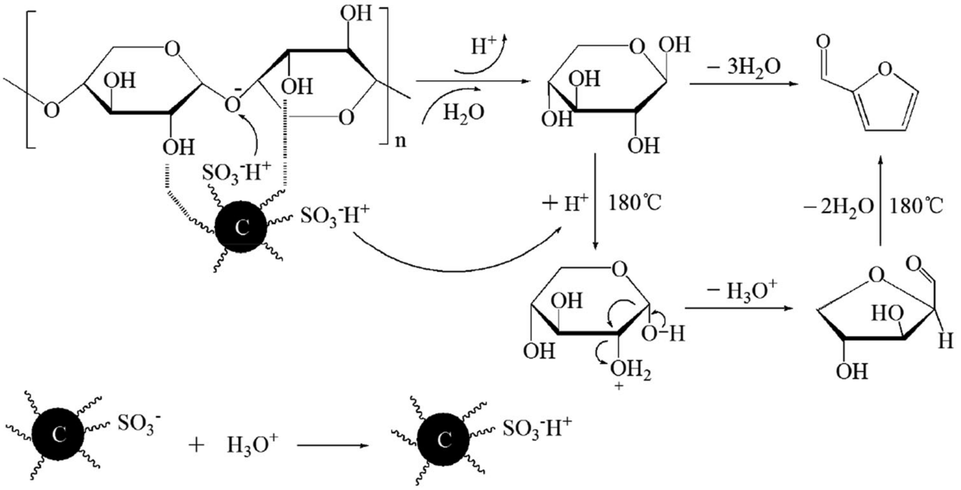

**Fig. 12** Suggested mechanism for catalytic degradation of corncob to furfural by biochar catalyst

shown in Fig. 12. The flexible carbon microspheres makes the biochar catalyst to be easily adsorbed to the corncob surface by hydrogen bonds among OH groups, and then the $SO_3H$ groups ($H^+$) can cleave β-1,4 glycosidic linkages in cellulose and hemicellulose effectively to water-soluble sugars, as well as to facilitate the dehydration of xylose and glucose to give furfural and a little HMF [34].

## Conclusions

In this work, a new furfural production process through corncob hydrolysis was investigated which uses biochar catalysts and recycles the hydrolysis degradation solution and solid residues. The suitable conditions for the preparation of biochar catalyst was the mixture component ratio of 1.5:90 (w/v) with lignocellulose residue to concentrated saccharide solution, then carbonized at a temperature of 180 °C for 48 h, and finally impregnated in 0.5 mol/L sulphuric acid at room temperature for 24 h assisted by the ultrasonic vibration.

Using the above-prepared biochar catalyst, corncob degradation was performed under the optimum operating condition as 5.0 g corncob, 0.4 g catalyst, 60 mL water at 180 °C for 170 min, the highest furfural yield of 37.75 % and total reducing sugars of 63.01 % were achieved which were much higher than the conventional process using the same feedstock (corncobs) and sulphuric acid. The most prominent advantage of the process is the full recycling of the degradation solution of corncob hydrolysis and part recycling of the lignocellulose residues.

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