



# Catalytic hydrolysis of corncob cellulosic polysaccharide into saccharides using $\text{SnO}_2\text{-Co}_3\text{O}_4/\text{C}$ biochar catalyst

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## Abstract

This paper presents hydrothermal decomposition of cellulosic polysaccharides in corncob using  $\text{SnO}_2\text{-Co}_3\text{O}_4/\text{C}$  biochar catalyst to nine soluble monosaccharides including xylose, mannose, galactose, glucose, xylulose, arabinose, fructose, maltose and sucrose.  $\text{H}_3\text{O}^+$  can convert hemicellulose and cellulose to soluble sugars by saccharification, following the Lewis acid sites from  $\text{SnO}_2\text{-Co}_3\text{O}_4\text{-2/C}$  catalyst make the isomerization of xylose to xylulose or arabinose, as well as glucose to fructose. The xylulose and fructose would be furthermore dehydrated to small compounds due to the acid strength of catalyst. Maltose and sucrose could be produced by the condensation of monosaccharides with prolonged reaction time. The maximum yield of reducing sugars reached 83.3% under the optimized operation condition as 5 g dried corncob particles, 0.3 g  $\text{SnO}_2\text{-Co}_3\text{O}_4/\text{C}$  biochar catalyst and 100 mL  $\text{H}_2\text{O}$  charged in the reactor at 180 °C for duration of 170 min.

**Keywords** Corncob · Cellulosic polysaccharide · Saccharification · Hydrothermal · Degradation ·  $\text{SnO}_2\text{-Co}_3\text{O}_4/\text{C}$  biochar catalyst

## Introduction

Biomass is one of the most abundant natural sources of carbon resources for the production of a wide range of chemicals with various applications [1–4]. Biomass (lignocellulosic) has a complex structure consists of cellulose, hemicelluloses and lignin. Agricultural lignocellulose is the most abundant and less expensive type of biomass on earth, therefore, being a promising feedstock for the production of renewable energy, especially biofuels, and chemicals [5]. Corncob is a by-product of the corn process industry that is traditionally used as livestock feed, firewood substitute, or rotted in the farmland. The major compositions of the corncob are about 38 wt% hemicelluloses, 35 wt% cellulose and 20 wt% lignin [6]. Hemicellulose is heteropolysaccharide

composed of different polysaccharides, such as mannans, xylans, arabinans, galactans and glucomannan. Cellulose is a homopolysaccharide composed of glucose units linked to each other through  $\beta$ -1-4-glucosidic bonds [7]. The biomass-derived starting materials have attracted much attention due to their convenient production from renewable sources [8–11]. Furfural, derived from hemicellulose, is a key platform compound which can be widely converted to a variety of chemicals and biofuels [12–15]. Hydrogenation is one of the potential routes for furfural conversion [16–21]. However, the furfural is produced not only by fructose conversion.

Lignocellulosic biomass materials are usually divided into monosaccharides, disaccharides, oligosaccharides and polysaccharides, wherein monosaccharides and disaccharides are commonly referred to sugars [22]. The past few decades have witnessed significant researches and development activities using different methods for hydrolysis and conversion hemicellulose and cellulose, such as mineral acids, bases and enzymes [23, 24]. Liquid acid-catalyzed hydrolysis of cellulose is efficient. However, corrosion, waste disposal and solvent recycle make this method unattractive.

Some attempts have been made on the hydrolysis of cellulose in ionic liquids since cellulose has good solubility

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in chloride and acetate anion ionic liquids. Zhou [25] reported that cellulose was degraded by  $WCl_6$  in 1-butyl-3-methyl imidazole chloride at 80 °C and lower, and 83% and 85.5% yield of total reducing sugar was obtained at 70 and 80 °C, respectively. Recently, sugarcane bagasse was pretreated with alkali and enzymatic delignification to be obtained de-lignified bagasse and then produced ethanol by saccharification and fermentation [26]. Daniel described the different methods of producing xylose, mannose, and arabinose sugars from hemicellulosic oligosaccharides of biomass by enzymatic and thermochemical pretreatments, and demonstrated that the oligosaccharides, such as xylo-oligosaccharides, arabinooligosaccharides and mannooligosaccharides have great potential from agricultural crop residues [27]. Ruppert had obtained the monosaccharide and disaccharides from carbohydrates by hydrogenolysis and hydrogenation [28]. In addition, some researcher works indicated that the contents of xylose and arabinose could be increased to 70% and 18%, respectively, by ionic liquid pretreatment to change the structure of hemicellulose from corncob [29]. Moreover, Liu demonstrated a novel and facile approach of conversion monosaccharides (glucose and xylose) to oligosaccharides [cello-oligosaccharides (COS) and xylo-oligosaccharides (XOS)], the yields of COS and XOS reached 4.62% (38 s) and 47.09% (30 s), respectively, at 500 °C reaction temperature coupled with sharp-quenching method [30]. Although these methods are improvements over the use of mineral acids alone, they are limited by the nature of the catalyst and its activity at the given conditions. Carbon materials derived from activated carbon, sugar or cellulose are solid acid catalysts that have the potential to eliminate many of the problem associated with solvent recycle and separation and can be made from renewable resources [31, 32].

In previous studies, we mainly investigated the process of furfural generation from cellulose. However, it was found that the furfural production process was not only through fructose. In this work, it is to produce soluble sugars by corncob hydrothermal degradation in the present of  $SnO_2-Co_3O_4/C$  biochar catalyst, which was prepared by sugar solution and lignocelluloses residue from corncob degradation, as well as mixture precipitated  $Sn(OH)_4$  and  $Co(OH)_2$ . There are few reports that nine kinds of sugars are obtained at the same time. It was included saccharification of hemicellulose and cellulose of corncob which produces a series of saccharides, and isomerization of xylose to xylulose or arabinose, as well as glucose to fructose. Meanwhile, it also found that there were condensation reactions of monosaccharide to disaccharide, and partly dehydration of monosaccharides to furfural (FF) or 5-hydroxymethylfurfural (HMF) along with the saccharification of corncob over  $SnO_2-Co_3O_4/C$  biochar catalyst.

## Experimental

### Material

Corn cob was supplied from a local farm located in Hebei Province, China. Corn cob was firstly chopped into small pieces and dried at 60 °C under vacuum for 24 h. Then, the dried corncob particles were sieved through 20 and 80 meshes to collect particles sized between 0.9 and 0.2 mm for experiments. Xylose, xylulose, arabinose, mannose, galactose, glucose, fructose, maltose and sucrose were supplied from Bioreagent Company, Shanghai, China. The chemicals and organic solvents used in experiments were all of the analytical grades and purchased from Tianjin Kermel Chemical Reagents Co. Ltd, China. Distilled water was used in the preparation of all solutions.

### Preparation of $SnO_2-Co_3O_4/C$ biochar catalyst

The amounts of 1.744 g  $SnCl_4 \cdot 5H_2O$  and 0.6 g  $CoCl_2 \cdot 6H_2O$  as the metal raw materials were used to prepare sol-gel  $Sn(OH)_4$  and  $Co(OH)_2$  mixture hydroxide. The sol-gel mixture hydroxide was directly added to 1.5 g lignocellulose residues and 150 mL degradation solution (containing 20.7 g soluble reducing sugars) and then concentrated to paste by rotary evaporation at 45 °C under 0.09 MPa absolute pressure. The paste carbonization was carried out in a tube-carbide furnace at 200 °C for 48 h with a nitrogen gas atmosphere. After cooling down to the ambient temperature, the carbonized solid mixture was ground into powder (60–80 meshes) to give the  $SnO_2-Co_3O_4/C$  biochar catalyst. With a similar procedure, a group of biochar catalysts such as  $SnO_2/C$ ,  $Co_3O_4/C$ ,  $SnO_2-SiO_2/C$ ,  $SnO_2-Al_2O_3/C$  and  $SnO_2-TiO_2/C$  were also prepared and employed to make comparison. In this work, there was no need to consider the recovery of biochar catalysts because they were utilized from lignocellulose residues to make new biochar catalyst in next cycle.

### Determination of acid density of $SnO_2-Co_3O_4/C$ biochar catalyst

The acid density of  $SnO_2-Co_3O_4/C$  biochar catalyst was estimated by neutralized titration method [33] as the following steps: 0.2 g of  $SnO_2-Co_3O_4/C$  biochar catalyst was added to 40 mL of 2 mol/L NaCl solution and stirred at room temperature for 24 h so that  $Na^+$  and  $H^+$  equilibrium on the catalyst surface was changed. After separation of the catalyst by filtration, the filtrate was titrated with 10 mmol/L NaOH solution. The acid density of  $SnO_2-Co_3O_4/C$  biochar catalyst was calculated using the following formulas, and the equivalent concentration of sulphuric acid employed in corncob hydrolysis was also determined by stoichiometric

proportion according to the acid density of  $\text{SnO}_2\text{-Co}_3\text{O}_4/\text{C}$  biochar catalyst.

$$\text{Acid density of catalyst} = \frac{CV}{m}, \quad (1)$$

$$\text{Concentration of sulphuric acid} = \frac{CV}{2M}, \quad (2)$$

where  $C$  is the concentration of NaOH solution,  $V$  is the volume of using NaOH solution,  $M$  is the relative molecular mass of sulphuric acid and  $m$  is the quality of  $\text{SnO}_2\text{-Co}_3\text{O}_4/\text{C}$  biochar catalyst.

### Catalytic hydrolysis of corncob

The catalytic hydrolysis of corncob was performed in a stainless steel batch autoclave equipped with a liner of

$$\text{Soluble sugar yield \%} = \frac{[\text{Soluble sugar}]_{\text{mass}}}{[\text{Hemicellulose} + \text{cellulose}]_{\text{mass fraction}} \times [\text{Charged corncob}]_{\text{mass}}} \times 100\%, \quad (3)$$

$$\text{Furfural yield\%} = \frac{[\text{Furfural}]_{\text{mass}}}{[\text{Hemicellulose}]_{\text{mass fraction}} \times [\text{Charged corncob}]_{\text{mass}}} \times 100\%, \quad (4)$$

$$\text{HMF yield\%} = \frac{[\text{HMF}]_{\text{mass}}}{[\text{Cellulose}]_{\text{mass fraction}} \times [\text{Charged corncob}]_{\text{mass}}} \times 100\%, \quad (5)$$

polytetrafluoroethylene. As a typical run, 5 g dried corncob particles, 0.1–0.4 g  $\text{SnO}_2\text{-Co}_3\text{O}_4/\text{C}$  biochar catalyst and 80–140 mL water were charged in the reactor, fasten the cover of autoclave and the mixture was then heated at 160–200 °C with a duration of 160–200 min in the oven. After the hydrolysis reactions, the mixture of corncob degradation solution and unreacted solid residue were separated by filtration. In this study, the effect of different operation conditions (time, temperature, catalyst dosage, the ratio of corncob to water) on the corncob hydrolysis to soluble sugars was investigated intensively.

### Product analysis and corncob conversion ratio

Based on the calibration curve, FF and 5-HMF concentration in the products of corncob degradation was determined quantitatively using a high-performance liquid chromatography (HPLC) instrument (LC-20AD, Shimadzu, Japan) equipped with a SPD-M20AV UV detector and an Inertsil

ODS-EP C18 reversed-phase column (4.6 × 250 mm) at 40 °C column temperature. In the measurement, a mixture of water and methanol (77:23, v/v) was 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 [34]. The analysis of compositions in the reducing sugar was performed using an HPLC instrument (LC-20AD, Shimadzu, Japan) equipped with an evaporative light scattering detector (ELSD) (Alltech LC-2000ES) and an XBridge BEH Amide Column (4.6 mm × 250 mm). The chromatograms of standard sugars mixture were also shown as reference. The pre-set chromatographic conditions are listed in Table 2.

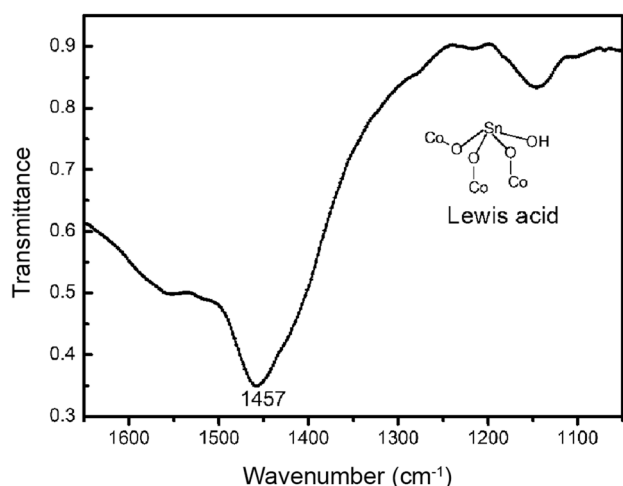
The yields of products and the corncob conversion ratio were calculated based on the following equations:

$$\text{Corncob conversion yield\%} = \frac{[\text{Reacted corncob}]_{\text{mass}}}{[\text{Total corncob}]_{\text{mass}}} \times 100\%. \quad (6)$$

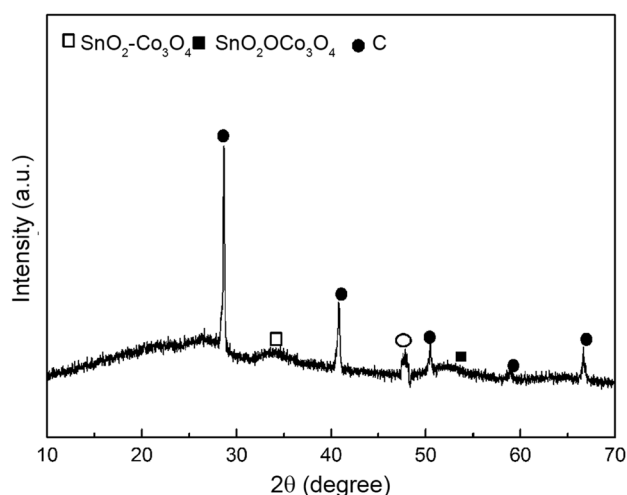
## Results and discussion

### Characterization of biochar catalyst

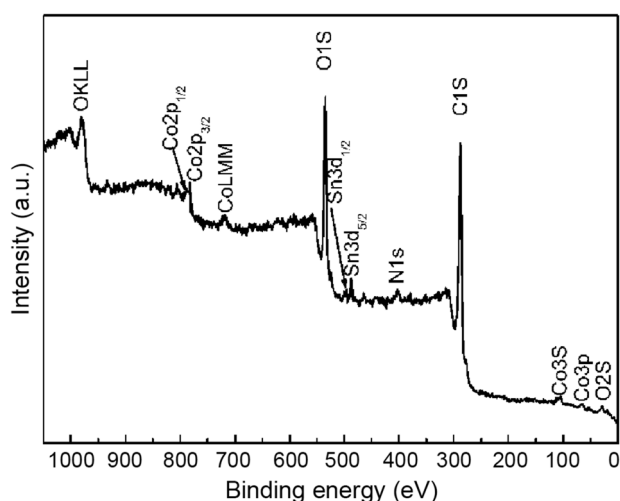
The determination of type (Brønsted or Lewis) of acid sites of the catalysts was performed by Fourier transform infrared (FTIR) spectroscopy combined with in situ adsorption of pyridine. The absorption bands appearing at 1545 and 1455  $\text{cm}^{-1}$  in the IR difference spectra were acceptedly assigned to adsorbed pyridinium ions and pyridine coordinated to Lewis acid sites, respectively [35]. The peak at 1457  $\text{cm}^{-1}$  was considered to relate to the characteristic vibrations of Lewis acid sites, as shown in Fig. 1. After  $\text{SnO}_2$  and  $\text{Co}_3\text{O}_4$



**Fig. 1** FTIR spectra of  $\text{SnO}_2\text{-Co}_3\text{O}_4\text{-2/C}$  catalyst after pyridine adsorption



**Fig. 3** XRD patterns of  $\text{SnO}_2\text{-Co}_3\text{O}_4\text{-2/C}$  catalyst

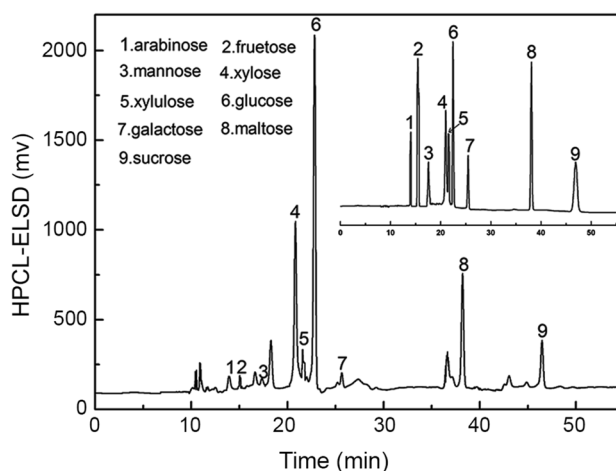


**Fig. 2** XPS spectra of  $\text{SnO}_2\text{-Co}_3\text{O}_4\text{-2/C}$  catalyst

loading on biochar carrier, the acid site of  $\text{SnO}_2\text{-Co}_3\text{O}_4\text{/C}$  biochar catalyst was changed from Brønsted acid to Lewis.

To identify the elemental compositions and chemical states of the product, X-ray photoelectron spectroscopy (XPS) analysis was carried out for  $\text{SnO}_2\text{-Co}_3\text{O}_4\text{-2/C}$  catalyst. Figure 2 shows the survey spectrum of Co, Sn and O elements in the region of 0–1000 eV. It was certain that the content of C and O was about 94%, and the remaining content was made up with N, Sn, Co and few Si. The  $\text{SnO}_2$  species were the main Sn species on the surfaces of the bimetallic  $\text{SnO}_2\text{-Co}_3\text{O}_4\text{-2/C}$  catalyst, and the  $\text{Co}_3\text{O}_4$  was also existed.

Figure 3 shows the X-ray diffraction (XRD) patterns of  $\text{SnO}_2\text{-Co}_3\text{O}_4\text{-2/C}$  catalyst. The diffraction peaks  $2\theta$  at  $31^\circ\text{--}36^\circ$  correspond to crystal planes of  $\text{Co}_3\text{O}_4$  and  $\text{SnO}_2$ . In addition, the diffraction peaks  $2\theta$  at  $21.5^\circ$ ,  $23.5^\circ$ ,  $35.2^\circ$ ,



**Fig. 4** HPCL-ELSD chromatograms of water-soluble sugars from corncob hydrolysis with  $\text{SnO}_2\text{-Co}_3\text{O}_4\text{/C}$  catalyst

$45.1^\circ$ ,  $53.3^\circ$ ,  $61.4^\circ$ ,  $68.7^\circ$  in the  $\text{SnO}_2\text{-Co}_3\text{O}_4\text{-2/C}$  catalyst can be indexed as carbon carrier. It indicates that there are more  $\text{SnO}_2$  and  $\text{Co}_3\text{O}_4$  particles attached to the biomass carrier.

### Corn cob saccharification

Lignocellulose could be hydrolyzed under acid conditions and produce arabinose, xylose, glucose and other compounds [36]. In the degradation solution of corncob hydrolysis over  $\text{SnO}_2\text{-Co}_3\text{O}_4\text{/C}$  biochar catalyst with Lewis acid

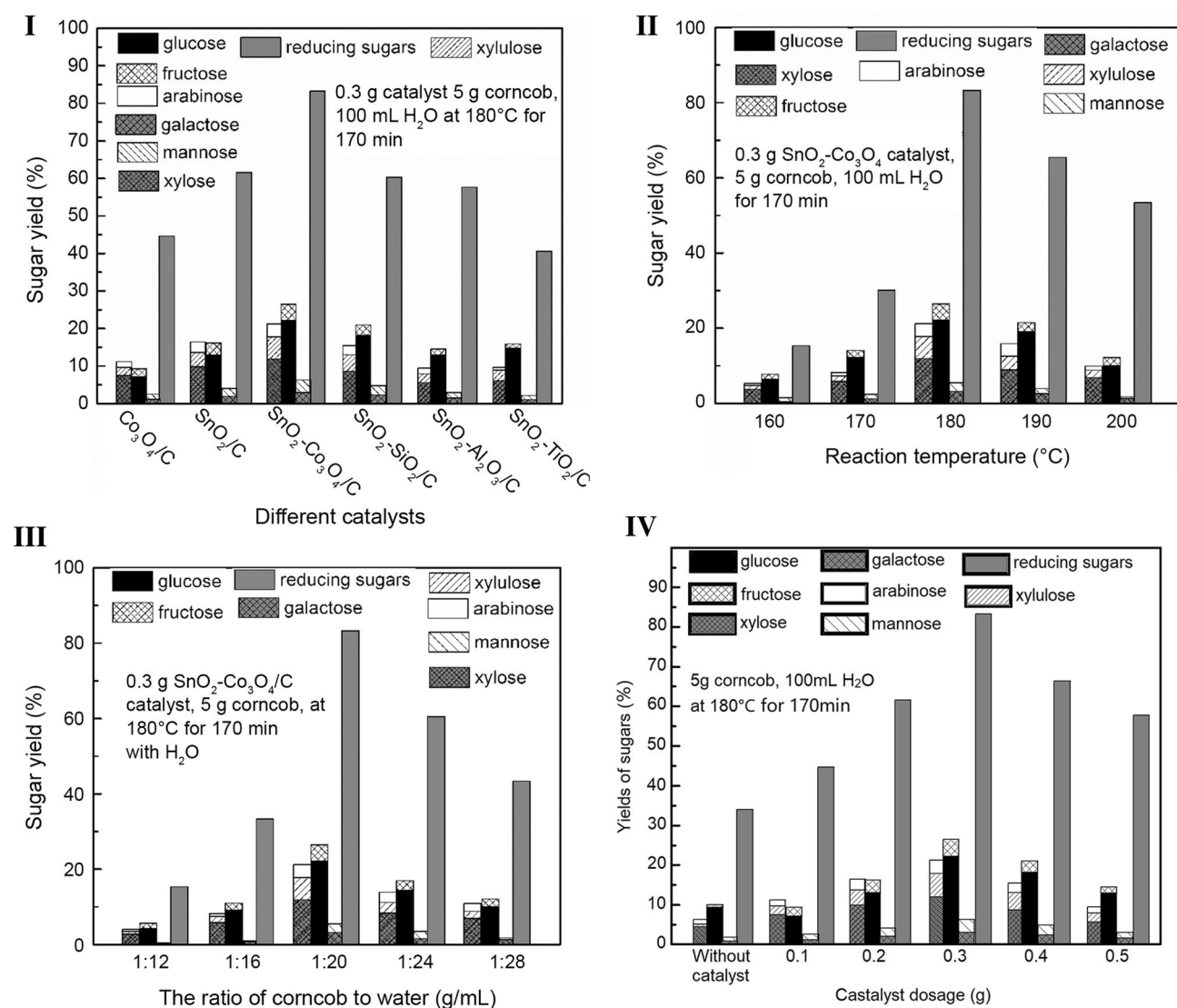
circumstance in water medium, nine sugar components were identified, as shown in Fig. 4. The chromatograms of nine standard sugars mixture were also shown as reference. There were also other unknown sugars from corncob hydrolysis.

In this work, the degradation solution contained about 83.3% reducing sugars was formed from the saccharification of hemicellulose and cellulose in corncob. The experimental data in Fig. 4 indicate that the glucose and xylose were the main products among monosaccharides, their contents were up to 34.1%. Because xylose could further be converted to xylulose or FF under the Lewis acid function [37], the content of glucose remained in degradation solution higher than that of xylose. It was demonstrated that the SnO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub>/C biochar catalyst was more suitable for cellulose and hemicellulose hydrolysis. In addition, the

disaccharide was also synthesized from the corresponding monosaccharide by condensation reaction.

### Optimized conditions for corncob saccharification with SnO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub>/C biochar catalyst

It has reported that acid strength has a significantly influence on corncob saccharification [38]. The aldose could be isomerized to ketose by Lewis acidity, and some metal oxides containing Sn (IV) were also regarded as a strong Lewis acid due to the availability of Lewis acid sites [39]. The effect of different biochar catalysts on the sugars yields is illustrated in Fig. 5I. The content of reducing sugars was the highest with 83.3% yield. The yields of monosaccharides, such as xylose, glucose, mannose and galactose



**Fig. 5** Effects of reaction factors on corncob saccharification. (I) different catalysts, (II) temperature, (III) ratio of corncob to water, and (IV) catalyst dosage

were 11.9%, 22.2%, 3.29% and 3.01%, respectively, when 0.3 g SnO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub>/C biochar catalyst was added in the reactor, compared with single SnO<sub>2</sub>/C and Co<sub>3</sub>O<sub>4</sub>/C catalyst. The BET surface area of SnO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub>-2/C catalyst was 6.338 m<sup>2</sup>/g and its acid density was 0.538 mmol/g. The SnO<sub>2</sub> played an important role in supplying Lewis acid sites on the surface of SnO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub>-2/C catalyst. There was a synergetic action between SnO<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub> for corncob hydrolysis. The elemental contents of Sn and Co in the SnO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub>-2/C catalyst were 391.43 and 90.24 µg/g by AAS analysis, respectively. However, the catalytic performance of SnO<sub>2</sub>-SiO<sub>2</sub>/C, SnO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>/C and SnO<sub>2</sub>-TiO<sub>2</sub>/C catalysts was not better than that of SnO<sub>2</sub>/C. Perhaps they were more suited to generate terminal products than saccharification process to give monosaccharides, such as FF, HMF, lactic acid, levulinic, ethanol, etc. [40, 41].

Figure 5II shows the yields of sugars which are dramatically increased with the reaction temperature from 160 to 180 °C. However, the enhancement of xylulose, arabinose and fructose yields were not high as compared with the reducing sugars. This was just according to a report by Vinit Chuhdhary who claimed that aldose isomerization to ketosis does not require much energy. It was proved that the corncob saccharification needed higher reaction temperature than isomerization [42].

The amount of catalyst has mainly affected the acidity of catalyst in the reaction of corncob saccharification. As shown in Fig. 5III, when the dosage of catalyst was 0.3 g, the catalytic effect was better and the yield of reducing sugar was up to 83.3%. The yield of monosaccharide increased with the amount of catalyst in the range of 0–0.3 g. The increased yield of xylose, arabinose and fructose is due to the isomerization of xylose and glucose under the SnO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub>/C catalyst. In addition, with the increase in the amount of catalyst, the yield of soluble sugar decreased, mainly because the increase of acidity converted the cellulose and semi-fiber in the corncob to other small molecular compounds.

The principle of cellulose hydrolysis could be described as the chemical formulation: (C<sub>6</sub>H<sub>10</sub>H<sub>5</sub>)<sub>n</sub> + n H<sub>2</sub>O → n (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>). It can be clearly seen in Fig. 5IV that the water volume and suitable ratio of corncob to water have a great effect on the corncob saccharification. When the amount of water was less than 16 mL per 1 g of corncob, the corncob saccharification was insufficient and the sugars yields were lower, even no mannose and galactose produced. Based on the hydronium ion H<sub>3</sub>O<sup>+</sup> from overstock water and hot temperature [43], the production of xylose and glucose decreased due to the isomerization to xylulose and fructose, respectively, and then FF and HMF were generated by dehydration.

Accompanied by the saccharification of corncob over SnO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub>/C biochar catalyst at temperature 180 °C for the duration of 160–200 min, it was also found that there

**Table 1** Effect of SnO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub>/C catalyst dosage, water and reaction time on the production of sugars

Time (min)	H <sub>2</sub> O (mL)	Catalyst dosage (g)	Conversion ratio (%)	Yields of products (%)										
				Xylose	Mannose	Galactose	Glucose	Xylulose	Arabinose	Fructose	Maltose	Sucrose	FF	HMF
160	80	0.4	40.6	3.93	0.71	0.89	7.59	1.08	0.86	1.16	1.00	0.93	6.18	4.81
170	100	–	35.2	4.38	0.96	0.78	9.32	0.82	1.13	0.68	0.77	0.64	5.07	2.17
170	120	0.2	45.4	13.9	3.65	3.78	25.2	1.08	0.98	1.18	1.01	1.49	12.9	3.91
170	100	0.3	48.2	11.9	3.29	3.01	22.2	5.89	3.42	4.25	2.79	2.11	15.8	8.54
170	100	H <sub>2</sub> SO <sub>4</sub> <sup>a</sup>	51.3	6.56	1.00	1.12	17.5	1.04	0.90	1.21	1.35	1.08	21.3	9.85
170	140	0.1	49.4	6.30	0.85	1.14	13.3	1.91	1.02	1.98	1.24	1.47	14.1	4.63
170	100	0.4	49.4	8.63	2.46	2.33	18.2	4.38	2.46	2.74	1.65	1.31	11.8	5.34
180	100	0.3	55.8	7.56	3.01	3.70	15.3	5.24	4.55	5.63	2.26	1.64	19.0	9.54
190	100	0.3	59.8	5.48	1.64	1.42	14.4	6.83	5.17	6.07	3.23	2.89	23.5	12.9
190	120	0.3	54.2	5.17	1.04	1.12	10.2	4.17	3.84	3.85	2.05	1.91	24.6	15.0
200	100	0.3	56.3	3.91	1.01	0.93	10.1	1.94	1.08	2.18	1.04	0.75	28.2	11.8
200	120	0.3	62.7	3.26	0.87	0.90	9.25	1.32	0.99	1.74	0.96	0.80	30.1	16.0
200	120	0.1	47.8	4.76	0.79	0.69	9.03	1.00	0.90	1.03	0.94	0.89	18.6	7.7

Reaction condition: 5 g corncob at 180 °C. H<sub>2</sub>SO<sub>4</sub><sup>a</sup> (98%) of 4.5wt% was used that has almost equivalent acidity to the SnO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub>/C catalyst

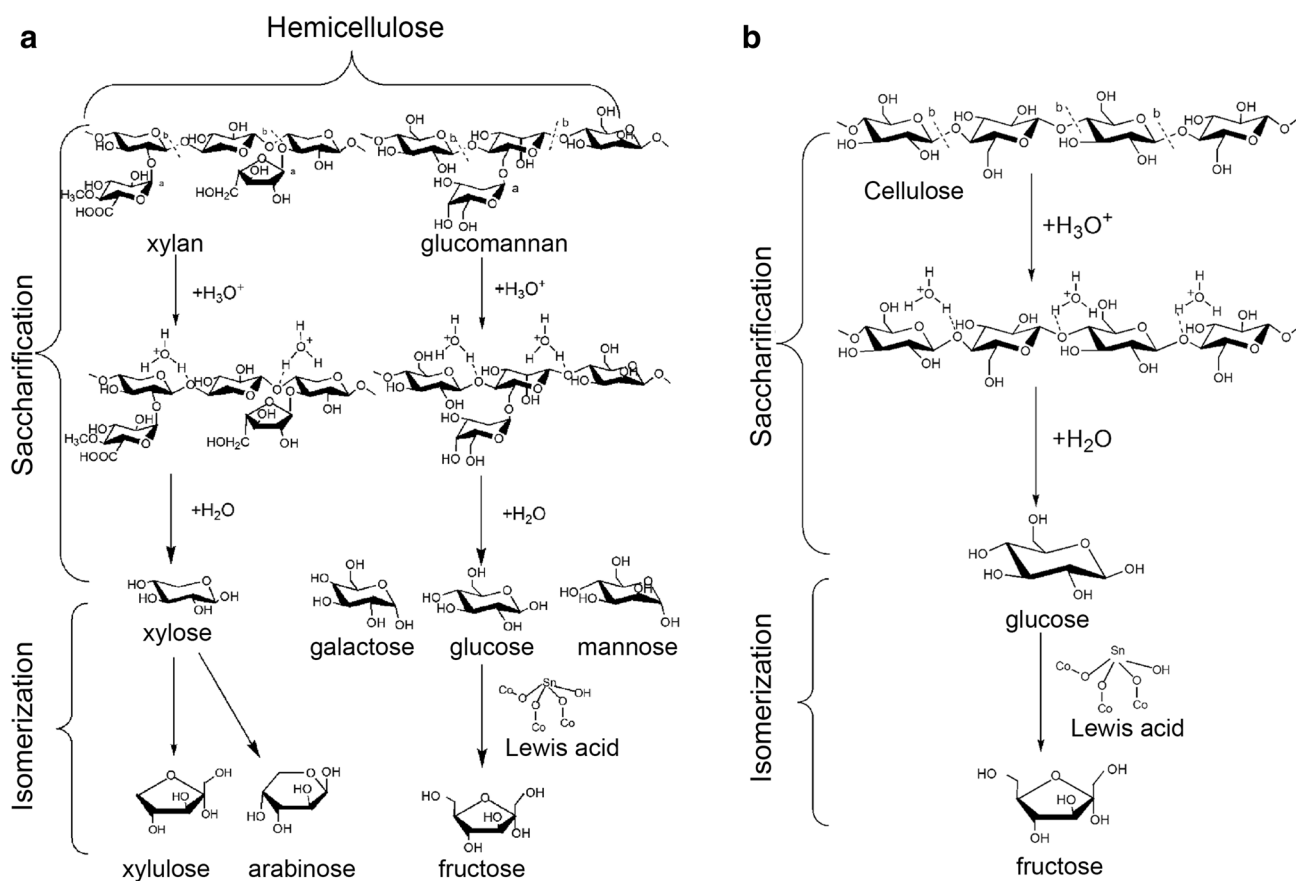
were isomerization, condensation and dehydration simultaneously. It can be seen that in Table 1 the yields of xylulose, arabinose and fructose were lower when 4.5 wt%  $\text{H}_2\text{SO}_4$  was employed as Brønsted acid catalyst, which had almost equivalent acidity to the  $\text{SnO}_2\text{-Co}_3\text{O}_4/\text{C}$  biochar catalyst (0.542 mmol/g). Beyond the corrosive action to instrument, the  $\text{H}_2\text{SO}_4$  could make the dehydration of xylose to FF and glucose to HMF directly. There was no isomerization reaction observed during corncob saccharification with  $\text{H}_2\text{SO}_4$  catalyst.

When corncob saccharification was performed under the optimum operation condition as 5 g corncob, 0.2 g  $\text{SnO}_2\text{-Co}_3\text{O}_4/\text{C}$  biochar catalyst and 120 mL  $\text{H}_2\text{O}$  at 180 °C for 170 min duration, the highest yields of xylose, mannose, galatose, glucose were 13.9%, 3.65%, 3.78%, 25.2%, respectively. The optimized condition for monosaccharides isomerization could give to xylulose (5.89%), arabinose (3.42%) and fructose (4.25%). The condensation reaction proceeded with the reaction time prolonged to 190 min with 0.3 g  $\text{SnO}_2\text{-Co}_3\text{O}_4/\text{C}$  biochar catalyst and 100 mL  $\text{H}_2\text{O}$  at 180 °C, and the yield of maltose and sucrose reached 3.23% and 2.89%, respectively.

## Saccharification and isomerization of corncob with $\text{SnO}_2\text{-Co}_3\text{O}_4/\text{C}$ biochar catalyst

The hemicellulose in corncob is a typical heterogeneous polymer constructed with pentose and hexose sugars [44], such as xylose, arabinose, glucose, galactose and mannose, etc. Cellulose is considered to be a major source of glucose, so it is readily available and renewable. Therefore, the saccharification was taken as a depolymerization of hemicellulose and cellulose to sugars by acidic hydrolysis. It is an interesting process especially for the production of rare sugars which are high value-added compounds in the future biorefinery. Daizo had employed carbon-based solid acid catalyst to catalytic conversion of starch to glucose and obtained the glucose yield of 77.54% [45]. Although there were only 13.9% xylose and 25.2% glucose by corncob saccharification with  $\text{SnO}_2\text{-Co}_3\text{O}_4/\text{C}$  biochar catalyst in our experiment, the final nine monosaccharides, as the special bio-energy resources, were made from cellulose and hemicellulose in non-food crop.

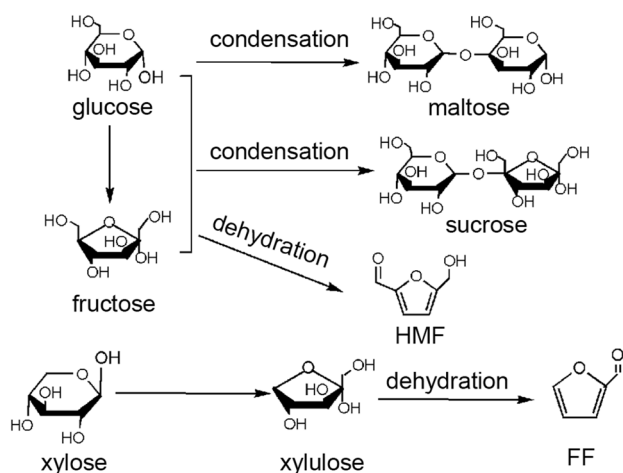
Typical simplified saccharification and isomerization reaction schemes of hemicellulose and cellulose are shown



**Fig. 6** a Supposed saccharification and isomerization reaction scheme of hemicellulose with  $\text{SnO}_2\text{-Co}_3\text{O}_4/\text{C}$  catalyst. b Supposed saccharification and isomerization reaction scheme of cellulose with  $\text{SnO}_2\text{-Co}_3\text{O}_4/\text{C}$  catalyst

**Table 2** 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 <sub>2</sub> O%				
0–40	90–80	10–20	95	2.0	off	1
40–50	80–90	20–10				
50–60	90	10				

**Fig. 7** Suggested pathway for condensation and dehydration of xylose and glucose

in Fig. 6a, b, respectively. The hemicellulose in corncob was saccharified to xylose by hydronium ion  $\text{H}_3\text{O}^+$  [40] under hydrothermal condition at temperature 180 °C. Then, Lewis acid sites on the surface of  $\text{SnO}_2\text{-Co}_3\text{O}_4\text{-2/C}$  catalyst facilitated the isomerization of xylose to xylulose that is an interconversion reaction with aldose to ketose of pentose sugars [46]. Because the aldose-ketose isomerization is a reversible reaction, the distribution of products was kept up with chemical equilibrium. For increasing the selectivity and yield of a monosaccharide, suitable reaction condition for saccharification and isomerization of corncob with  $\text{SnO}_2\text{-Co}_3\text{O}_4\text{/C}$  biochar catalyst is indispensable. As Table 2 shows, when 5 g corncob, 0.2 g  $\text{SnO}_2\text{-Co}_3\text{O}_4\text{/C}$  biochar catalyst and 120 mL  $\text{H}_2\text{O}$  were charged in the reactor and the corncob was hydrolyzed at 180 °C for 170 min duration, the total yield of monosaccharides was up to 49.77% and disaccharides was only 2.5%.

### Condensation and dehydration of monosaccharide with $\text{SnO}_2\text{-Co}_3\text{O}_4\text{/C}$ biochar catalyst

Xylose and glucose, as the raw material of biomass-based chemicals, were correspondingly converted to FF and HMF under acidity circumstance by dehydration [47]. The suggested pathway of condensation and dehydration of xylose and glucose, which were the products of corncob

degradation by hydrothermal process with  $\text{SnO}_2\text{-Co}_3\text{O}_4\text{/C}$  biochar catalyst, is illustrated in Fig. 7. The hydronium ion  $\text{H}_3\text{O}^+$  from hot water provides weak acidity, so the yields of FF and HMF are improved with the increasing volume of water. As shown in Table 2, the highest yields of FF and HMF have reached 30.1% and 16.0% with 5 g corncob, 0.3 g  $\text{SnO}_2\text{-Co}_3\text{O}_4\text{/C}$  biochar catalyst and 120 mL water at 180 °C for 200 min duration. Meanwhile, two molecules of glucose could couple to maltose by condensation reaction under acidic catalysis, like glucose and fructose coupling to sucrose. That was the reason why the content of sucrose and maltose increased with the longer reaction time. When 5 g corncob, 0.3 g  $\text{SnO}_2\text{-Co}_3\text{O}_4\text{/C}$  biochar catalyst and 100 mL  $\text{H}_2\text{O}$  were charged in the reactor and the corncob was hydrolyzed at 180 °C for 190 min duration, the total yield of maltose reached 3.23% and sucrose was 2.89%.

The validation experiment for preparation of furfural, as a comparison with  $\text{H}_2\text{SO}_4$  catalyst, was performed, and the yield of furfural was only 6.8% with the same content of  $\text{SnO}_2\text{-Co}_3\text{O}_4\text{/C}$  biochar catalyst. The experimental results indicated that the  $\text{SnO}_2\text{-Co}_3\text{O}_4\text{/C}$  biochar catalyst was more suitable for saccharification of hemicellulose and cellulose, as well as for isomerization of xylose to xylulose, rather than dehydration of xylulose.

## Conclusion

This study investigated a hydrothermal process for efficient conversion of corncob into reducing sugars (as much as 3.04 g/5 g corncob) using  $\text{SnO}_2\text{-Co}_3\text{O}_4\text{/C}$  biochar catalyst. After optimizing the hydrolysis parameters at 180 °C for 170 min, the total yield of monosaccharides was up to 49.77% and a maximum level of 13.9% xylose, 3.65% mannose, 3.78% galactose and 25.2% glucose were produced. There were also xylulose, arabinose and fructose in products as isomerization reaction of aldose to ketose during corncob saccharification with  $\text{SnO}_2\text{-Co}_3\text{O}_4\text{/C}$  biochar catalyst. The advantage of this process was hydrolysis of cellulose and hemicellulose in corncob to soluble sugars without conflicting food crop (cornstarch), and the degradation solution containing monosaccharides had no acidic properties and did not corrode the instrument.



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