

Bamboo-derived Magnetic Carbonaceous Solid Acid Catalyst for the Conversion of Corncob into Furfural Promoted by Warm Water Immersion

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In this study, a bamboo-derived magnetic carbonaceous solid acid catalyst (BC@Fe₃O₄@SO₃H) was synthesized by FeCl₃ impregnation, which was followed by incomplete carbonization and -SO₃H group functionalization. FT-IR, XRD, and TGA results showed that the prepared catalyst contained -SO₃H, -COOH, and phenolic -OH groups. It exhibited poor adsorption ability for the dominating sugars released during the catalytic conversion process. The prepared bamboo-derived magnetic carbonaceous solid acid presented high catalytic activity for depolymerization and conversion of corncob hemicellulose. Warm water immersion under 60 °C was able to destroy the complex corncob cell wall structure and accelerated the dissolution of carbohydrates. The highest furfural yield of 54.1 mg/g was obtained from 40 °C water-immersed corncob after reacting at 180 °C for 30 min. Up to 96.1% of the corncob hemicellulosic backbone sugars were depolymerized to monosaccharides and oligosaccharides in the hydrolysates. The prepared catalyst exhibited a simple magnetic recovery process and high stability. This work provides promising strategies for biomass utilization *via* renewable materials.

Keywords: Bamboo; Magnetic carbonaceous solid acid; Warm water immersion; Hemicelluloses; Furfural

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INTRODUCTION

The global energy crisis and environmental concerns about greenhouse gas emissions have stimulated the production of fuels, chemicals, and energy from renewable resources (Schneider *et al.* 2016). Lignocellulosic biomass is widespread, abundant, diverse, and inexpensive, and has been intensively investigated as a highly sustainable carbon-containing source for the production of bio-platform molecules and biochemicals (Li *et al.* 2015b; Cai *et al.* 2016). Upgrading lignocellulosic biomass to advanced biofuels and biochemicals is of particular importance for replacing traditional fossil fuels.

As an agricultural waste residue, corncob is available in immense quantities in China. In light of its high hemicellulose content, corncob is considered to be a feasible feedstock for producing a variety of valuable platform chemicals, such as xylose, furfural, and xylooligosaccharides. Furfural, which can be obtained from the dehydration of xylose, is a typical sylvichemical product that can be used to produce many important non-petroleum-derived chemicals based on its tunable functional groups (Wang *et al.* 2017).

The market demand for furfural is expected to reach 1100 million lb by 2020 (Sadula *et al.* 2017). However, inefficient strategies, equipment corrosion, and waste disposal have strongly limited its commercial competitiveness with petroleum-based alternatives. Therefore, the development of efficient and cost-effective catalytic reaction systems for furfural production and lignocellulosic biomass conversion has received much attention in recent years.

Furfural is commercially synthesized from lignocellulosic biomass *via* mineral acid catalysts by the depolymerization of biomass xylans into xylose and dehydration of xylose into furfural (Yemiş and Mazza 2011; Sadula *et al.* 2017). Furfural is a platform chemical that can be used to produce more than 80 high commercial value products, such as 2-methylfuran, furfuryl alcohol, tetrahydrofuran and various cyclo-products (Dimasrivera *et al.* 2014; Yan *et al.* 2014; Dalvand *et al.* 2018). The major disadvantages associated with the use of mineral acids include equipment corrosion, difficult recovery, and treatment of the acidic waste (Liu *et al.* 2012). Therefore, new innovative technologies and sustainable solutions using heterogeneous catalysts are required to overcome the handicaps of mineral acids.

To date, many types of heterogeneous acid catalysts, such as H-zeolites (Fan *et al.* 2017), metal oxides (Li *et al.* 2014a), ion-exchange resins (Mittal *et al.* 2017), and supported heteropoly acids (Cotta *et al.* 2017), have been tested for the direct conversion of biomass into biofuels and biochemicals. Compared with conventional solid acid catalysts, magnetic solid acids combine the properties of magnetism and acidity, and have drawn increasing attention in recent years because of their high catalytic performance, enhanced stability, and reusability (Huang and Fu 2013). Li *et al.* (2018) used magnetic biomass-based solid acid to catalyze the pyrolysis of corn straw. Results showed that the prepared catalyst exhibited high catalytic activity for the conversion of corn straw into levulinic acid. Moreover, the magnetic property of the catalyst allows for easy separation from pyrolysis residues. Chen *et al.* (2018) prepared a series of carbonaceous solid acids from biorenewable feedstocks and used them as catalysts for the direct conversion of carbohydrates into 5-ethoxymethylfurfural (EMF). Results showed that the prepared catalysts presented porous structure, high acid density, and easy separation. 63.2% EMF yield could be obtained from fructose at 120 °C. Magnetic solid acid materials have the characteristic of easy separation from reaction systems. Moreover, the preparation of magnetic solid acids by incomplete carbonization of lignocellulosic biomass and the subsequent sulfonation of the resulting carbon is a possible strategy for converting biomass *via* renewable materials.

Bamboo is a fast-growing perennial herbaceous plant with a large phytomass. China has long been known as the “Kingdom of Bamboo” and has more than 500 bamboo species over 39 genera (Li *et al.* 2015c; Cai *et al.* 2017). However, a lot of bamboo materials is wasted. Bamboo carbon (BC), a product obtained from the carbonization of bamboo, possesses various fascinating characteristics, such as a porous structure and high thermal stability (Li *et al.* 2017). These properties make BC an ideal precursor for producing solid acids.

Corn cob is a common agricultural waste that was widely used to produce platform chemicals, such as furfural, levulinic acid, and *etc.* (Li *et al.* 2015a; Ji *et al.* 2017). In this study, a bamboo-derived magnetic carbonaceous solid acid (BC@Fe₃O₄@SO₃H) with a unique magnetic core-shell and high acid content was prepared by the impregnation-incomplete carbonization-sulfonation method and used as a magnetic solid acid for a one-pot conversion of corn cob into furfural. The BC support is expected with porous structure

for the impregnation of FeCl_3 and H_2SO_4 , forming layers of adsorbate molecules which can interact with reactants (Kapoor *et al.* 1989; Rege and Yang 2010; Ghashghaee and Karimzadeh 2011). Physical and chemical properties of the prepared materials were investigated, and the effects of warm water immersion on corncob deconstruction were determined. The catalytic activity and stability of the prepared solid acids were also evaluated.

EXPERIMENTAL

Materials

Bamboo was collected from Hunan Province, China. Prior to the experiments, the bamboo was decorticated, ground, and sieved to an 80-mesh size. The obtained particles were oven-dried at 55 °C to a constant weight. The compositional analysis (glucose, xylose, arabinose, and lignin) of the bamboo was performed according to an established National Renewable Energy Laboratory procedure (Sluiter *et al.* 2010) with a resulting composition of 49.1 wt.% glucose, 14.0 wt.% xylose, 0.6 wt.% arabinose, and 37.1 wt.% lignin.

The corncobs used in this study were obtained from Shandong Province, China. Before the experiments, the corncobs were ground to pass through a 40-mesh screen, and then they were dewaxed with a 2:1 (v/v) acetone/ethanol mixture in a soxhlet extractor (1000 mL, Synthware Glass Co. Ltd., Beijing, China) for 6 h. The dewaxed corncob was oven-dried at 60 °C to a constant weight and milled for 6 h (300 rpm) with a ball-milling machine (DECO-PBM-V, Deco Co. Ltd., Hunan, China). The composition of the dewaxed corncob was 38.1 wt.% glucose, 31.9 wt.% xylose, 4.2 wt.% arabinose, and 25.8 wt.% lignin.

The chemicals $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (AR, $\geq 99.0\%$), H_2SO_4 (AR, 98.0%), and ethanol (AR, $\geq 99.0\%$) were purchased from Kermel Co. Ltd. (Tianjin, China). Standard reagents, including glucose ($\geq 99.0\%$, HPLC), xylose ($\geq 99.0\%$, HPLC), arabinose ($\geq 98.0\%$, HPLC), formic acid (50%, HPLC), acetic acid ($\geq 99.9\%$, HPLC), furfural ($\geq 99.0\%$, HPLC), and 5-hydroxymethylfurfural (HMF; $\geq 99.0\%$, HPLC), were purchased from Shanghai Sigma-Aldrich Trading Co. Ltd. (Shanghai, China). Xylobiose (X2; $\geq 95.0\%$, HPLC) and xylotriose (X3; $\geq 95.0\%$, HPLC) were obtained from WAKO (Wako, Japan). Xylooligosaccharides with a degree of polymerization (DP) of 4 to 6 (X4, X5, and X6) and a purity greater than or equal to 90.0% were purchased from Megazyme (Wicklow, Ireland). Deionized (DI) water was used to prepare all of the solutions. All of the chemicals were used as received.

Methods

Preparation of bamboo-derived magnetic carbonaceous solid acid

The $\text{BC@Fe}_3\text{O}_4\text{@SO}_3\text{H}$ was prepared with the impregnation-incomplete carbonization-sulfonation method, according to previously reported methods (Kitano *et al.* 2009; Zhang *et al.* 2013; Hu *et al.* 2015). Initially, 5.0 g of bamboo powder was dispersed in 500 mL of the $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ solution (100 mmol/L) and then stirred at room temperature (150 rpm) for 5 h. After that, the water in the mixture was evaporated out under reduced pressure, and the remaining solid was dried at 100 °C overnight in a vacuum oven. The obtained FeCl_3 -impregnated bamboo was carbonized at 500 °C for 1 h under a nitrogen atmosphere to produce the $\text{BC@Fe}_3\text{O}_4$ precursor.

The BC@Fe₃O₄@SO₃H catalyst was synthesized by the sulfonation of the BC@Fe₃O₄. Briefly, the BC@Fe₃O₄ was mixed with a concentrated sulfuric acid at a ratio of 1:10 (g/mL) and sonicated for 15 min. Subsequently, the mixture was heated under vigorous stirring at 90 °C for 10 h to introduce the sulfo-group (-SO₃H) to the surface of the magnetic BC. After the reaction, the mixture was cooled to room temperature and diluted with DI water. The solid product (BC@Fe₃O₄@SO₃H) was collected with a magnet and washed with DI water until no sulfate ions (SO₄²⁻) were detected in the filtrate. Finally, the resulting catalyst (BC@Fe₃O₄@SO₃H) was washed with ethanol and dried in a vacuum oven at 80 °C for 12 h.

Procedure for corncob conversion

The corncob conversion was conducted in a 100-mL high pressure batch reactor (SLM-100, Shenlang Co. Ltd., Beijing, China). In a typical experiment, 1.0 g of milled corncob and 20.0 mL of DI water were added into the reactor with a catalyst dosage of 0.2 g. The mixture was heated to the desired temperature over a certain time period with a magnetic stirring rate of 300 rpm. When the reaction temperature and time reached the preset values, the reactor was cooled with flowing water. The hydrolysate was filtered with a 0.22- μ m syringe prior to analysis with high-performance liquid chromatography (HPLC). The solid residues were washed with DI water several times and oven-dried at 60 °C to a constant weight. The magnetic solid acid BC@Fe₃O₄@SO₃H catalyst and corncob residue were separated by magnetism and stored in a desiccator until the subsequent analyses. To evaluate the recyclability of the prepared catalyst, the separated solid acid was impregnated with concentrated sulfuric acid in the manner described above and reused for the corncob conversion. Each experiment was repeated three times to ensure the reproducibility of the results, and the average value was reported.

Catalysts characterization

The Fourier-transform infrared (FT-IR) spectrum of the as-prepared BC@Fe₃O₄@SO₃H was recorded on a spectrophotometer (Tensor 27, Bruker Optics, Karlsruhe, Germany) over the range of 4000 cm⁻¹ to 400 cm⁻¹. The X-ray diffraction (XRD) patterns of the prepared catalysts were detected in the 2 θ range of 5° to 40° on a Bruker D8 ADVANCE X-ray diffractometer (Karlsruhe, Germany) with Cu K α radiation. The thermostability of the samples was tested with thermogravimetric analysis (TA Q200, New Castle, USA). The surface morphology of the warm water-immersed corncob was analyzed with scanning electron microscopy (SEM; S-4300, Hitachi, Tokyo, Japan). An acid-base titration test was performed to verify the free hydrogen ion (H⁺) concentration in the BC@Fe₃O₄@SO₃H. In briefly, 0.1 g catalyst was added into 20 mL NaCl solution (2.0 mol/L), and then stirred for 24 h (100 rpm) at room temperature. Subsequently, the mixture was filtered, liquid fraction (5 mL) was titrated with 50 mmol/L NaOH solution. Phenolphthalein was used as the indicator. Experiments were done in triplicate, and the average value was obtained.

Product analysis

The yields of xylose, glucose, arabinose, formic acid, acetic acid, furfural, HMF, and oligosaccharides with different polymerization degrees (DP = 2 to 6) in the liquid products were analyzed with HPLC (Model 2498, Waters, Milford, CT, USA) equipped with a refractive index detector (RID) and ultraviolet (UV)-RID. Two HPLC columns with the following specifications were used for the analysis of the different products: a Shodex

sugar SH-1011 column (Showa Denko, Tokyo, Japan) operating at 50 °C with a mobile phase of 5 mM H₂SO₄ at a flow rate of 0.5 mL/min was used for detection of the xylose, glucose, arabinose, formic acid, and acetic acid with the RID, whereas the detection of the furfural and HMF was done using the UV-RID; and an Aminex HPX-42A column (BioRad, Hercules, CA, USA) operating at a column oven temperature of 85 °C with DI water as the mobile phase at a flow rate of 0.2 mL/min was used for detection of the xylooligosaccharides (DP = 2 to 6) using the RID. Calibration curves of the different products were established for the quantitative calculation.

The carbohydrates and lignin in the treated corncob were analyzed according to Sluiter *et al.* (2010). In brief, the oven-dried treated samples (300 mg) were hydrolyzed with 72% H₂SO₄ (3 mL) at room temperature for 1 h. Subsequently, the hydrolysates were diluted with 84 mL of DI water and a second hydrolysis was performed at 121 °C for 1 h in an autoclave. After the reaction, the mixtures were filtered, and the solid residues were regarded as the acid-insoluble lignin. The neutral sugars in the hydrolysates were quantified with HPLC as was described earlier. The acid-soluble lignin was measured with a UV spectrophotometer (UV-1800, Shimadzu, Kyoto, Japan). The lignin content was the sum of the acid-soluble lignin and acid-insoluble lignin. All of the experiments were done in duplicate, and the average values were reported.

RESULTS AND DISCUSSION

Characterizations of the Catalysts

The FT-IR spectrum of the BC@Fe₃O₄@SO₃H is shown in Fig. 1. The typical band that appeared at 588 cm⁻¹ was assigned to the Fe-O vibration in Fe₃O₄ (He *et al.* 2008; Deng *et al.* 2016), whereas the weak band at 653 cm⁻¹ was from the S-O stretching mode (Xiong *et al.* 2014).

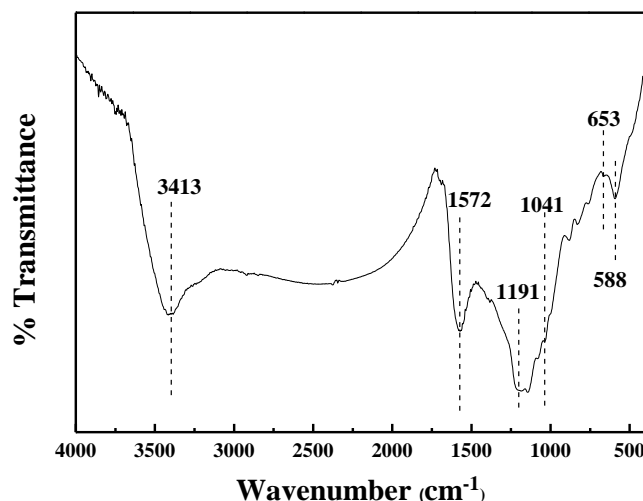


Fig. 1. FT-IR spectrum of the BC@Fe₃O₄@SO₃H

The bands at 1041 cm⁻¹ and 1191 cm⁻¹ were attributed to the O=S=O asymmetric and symmetric stretching vibrations, respectively. The presence of O=S=O typical peaks indicated that -SO₃H groups were successfully introduced into the prepared carbon

materials (BC@Fe₃O₄) (Liu *et al.* 2012). The sulfonic group shows interesting activity in biomass conversion (Maldonado *et al.* 2017). The peak at 1572 cm⁻¹ was from the C=C stretching vibration in aromatic carbons, and the band at 3413 cm⁻¹ was assigned to the O-H stretching vibration in -COOH and phenolic -OH groups that were generated during the carbonization and sulfonation process (Hu *et al.* 2015). The FT-IR pattern of the synthesized BC@Fe₃O₄@SO₃H was in agreement with the patterns reported in the literature (Xiong *et al.* 2014).

A sulfonation process was applied to the BC@Fe₃O₄ to produce the solid acid BC@Fe₃O₄@SO₃H. The crystalline structures of the BC@Fe₃O₄ and BC@Fe₃O₄@SO₃H were characterized by XRD, and the results are shown in Fig. 2. Samples were ground in an agate mortar to obtain fine particles. The observed sharp peaks at 2θ values of 30.0° and 35.3° were assigned to the (220) and (311) lattice planes of Fe₃O₄ (JCPDS19-629) (Qi *et al.* 2009; Hu *et al.* 2015). The XRD patterns of the prepared catalysts demonstrated that the magnetic iron oxide structure was well kept in the solid acid after -SO₃H functionalization.

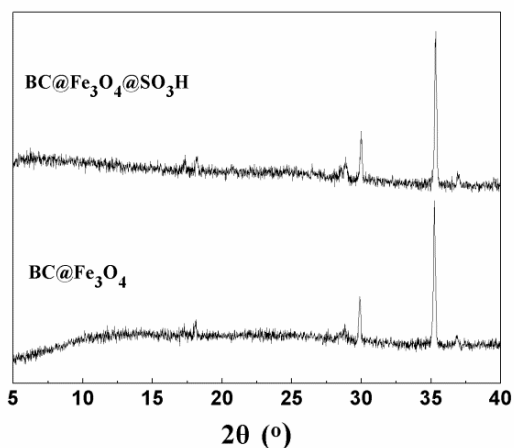


Fig. 2. XRD patterns of the BC@Fe₃O₄ and BC@Fe₃O₄@SO₃H

The mass loss and thermal behavior of the BC@Fe₃O₄@SO₃H under high temperatures are shown in Fig. 3. The thermal decomposition of the prepared BC@Fe₃O₄@SO₃H can be divided into three stages. The weight loss that occurred before 150 °C was mainly because of the evaporation of water adsorbed onto the surface of the BC@Fe₃O₄@SO₃H (Hu *et al.* 2015). The second weight loss stage from 200 °C to 400 °C corresponded to the decomposition of -SO₃H groups (Guo *et al.* 2013). The final stage that occurred above 400 °C was attributed to the further condensation of amorphous carbons (Hu *et al.* 2015). Moreover, about 8.7% weight loss of Fe precursor may be occurred between 180 °C and 500 °C, which may be ascribed to the decomposition and conversion reaction of Fe species of the catalyst at high temperatures (Dimas-Rivera *et al.* 2017).

During the carbonization process at a relatively high temperature, carbohydrates in lignocellulosic biomass begin to decompose, which leaves behind a rigid carbon skeleton in the form of aromatic sheets and strips (Rodríguez-Reinoso and Molina-Sabio 1992). Catalysts produced from lignocellulosic biomass are thought to be superior at adsorbing low molecular weight products because of the potential formation of hydrogen bonds (Hu *et al.* 2014). Therefore, monosaccharides, such as xylose, glucose, and arabinose, which are the major products used for hydrothermal conversion, were used to confirm this

conjecture (Fig. 4). In brief, 0.1-g samples of BC@Fe₃O₄@SO₃H were added to separate 2-mL aliquots containing xylose, glucose, and arabinose solutions (50 mg/mL). The mixtures were oscillated at room temperature for 0 min to 90 min, and the monosugars content in the liquid was measured by HPLC. The purpose of the experiment is to evaluate whether BC@Fe₃O₄@SO₃H will continue to adsorb monosaccharides at the end after the reaction.

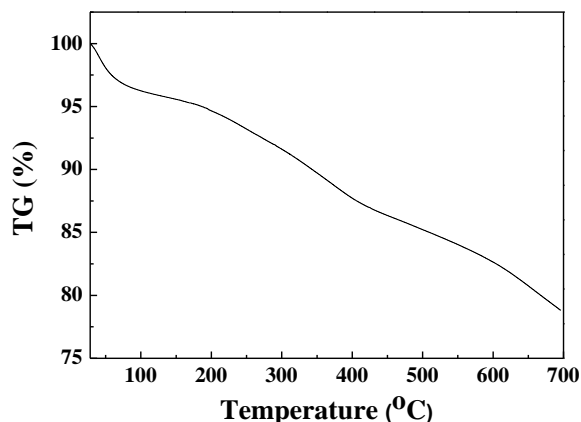


Fig. 3. Mass loss and thermal behavior of the BC@Fe₃O₄@SO₃H at high temperatures

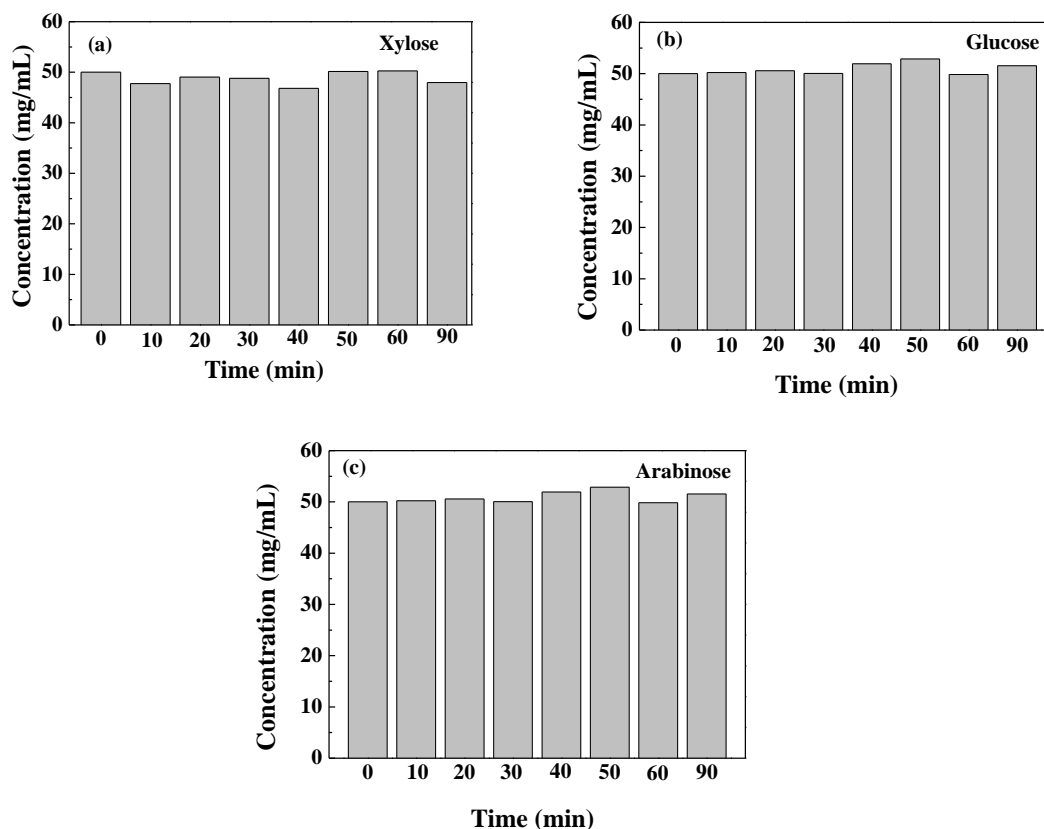


Fig. 4. Change in the concentrations of xylose (a), glucose (b), and arabinose (c) over 90 min

Figure 4 shows that the xylose, glucose, and arabinose concentrations barely changed over 90 min. This phenomenon suggested that the prepared BC@Fe₃O₄@SO₃H catalyst exhibited a poor adsorption ability for the dominating sugars released during the catalytic hydrothermal conversion process, which would cause less loss at the beginning and end of the reactions. The poor sugar adsorption ability of BC@Fe₃O₄@SO₃H can effectively diminish the HPLC analysis errors.

Influence of Different Catalysts on the Conversion of Corncob

Acidic catalysts provide a stable and sustainable catalytic performance for the conversion of lignocellulosic biomass. The potential of several acid catalysts in the decomposition and conversion processes of corncob carbohydrates were analyzed and the results are shown in Table 1. The liquid products were analyzed as was described previously.

Table 1. Product Distribution for the Conversion of Corncob with Different Catalysts

Entry	Catalyst	Xylose	Glucose	Arabinose	Formic Acid	Acetic Acid	Furfural	HMF
1	---	47.6	15.0	7.4	13.2	26.8	29.0	6.4
2	BFS	63.7	41.7	11.2	13.2	33.8	50.7	17.3
3	BF	47.6	41.0	12.4	9.1	35.1	38.7	15.6
4	H ₂ SO ₄	110.9	70.1	18.4	10.3	34.5	39.9	17.2
5	Amberlyst-15	109.7	106.7	20.5	12.9	35.4	32.9	14.4
6	Zeolite	41.2	14.1	14.0	6.5	35.1	49.6	7.8

Values are in mg/g; Reaction conditions: 1.0 g of corncob, 0.2 g of catalyst, 20 mL of DI water, 180 °C, 30 min, and 300 rpm; BFS: BC@Fe₃O₄@SO₃H; BF: BC@Fe₃O₄

Compared with the catalyst-free reaction (Table 1, Entry 1), the productivities of the monosaccharides (xylose, glucose, and arabinose), acids (formic acid and acetic acid), furfural, and HMF increased in the presence of catalysts (Table 1, Entries 2 to 6). This result indicated that acid catalysts could accelerate not only the hydrolysis of carbohydrates into oligosaccharides and monosugars, but also the dehydration of monosaccharides into furan compounds and cause further decomposition of furfural and HMF into organic acids. When zeolite was used as the solid acid catalyst for corncob conversion under the tested conditions, a poor monose yield of 69.3 mg/g was obtained with a relatively high furfural productivity of 49.6 mg/g (Table 1, Entry 6). Amberlyst-15 is a typical strong Brønsted acid catalyst, and 32.9 mg/g of furfural was produced with a monosaccharides yield of 236.9 mg/g, which was remarkably higher than the yields obtained from the other tested catalysts. The catalytic activity of the Amberlyst-15 was comparable to that of the dilute sulfuric acid (Table 1, Entry 4). These results were in agreement with the reaction state that the conversion of hemicellulose into furfural relies on both the Brønsted and Lewis acids (Li *et al.* 2015a). However, both had a lower catalytic performance than the prepared BC@Fe₃O₄@SO₃H in terms of the furfural production.

The number of H⁺ sites in the BC@Fe₃O₄@SO₃H was determined to be 1.69 mmol/g, which was based on the acid-base titration (Balikova 1975). Therefore, dilute sulphuric acid with a concentration of 8.45 mmol/L was used for comparison (Table 1, Entry 4). The H⁺ content in the dilute sulphuric acid was controlled so that it was the same as that of the BC@Fe₃O₄@SO₃H. Table 1 shows that although a higher xylose yield (110.9

mg/g) was obtained from the dilute H₂SO₄-catalyzed reaction, the highest furfural yield of 50.7 mg/g was achieved when using BC@Fe₃O₄@SO₃H as the acid catalyst under the tested conditions. This result indicated a favorable catalytic performance of the prepared magnetic solid acid. These results may be ascribed to the fact that the number of free H⁺ in the H₂SO₄ was higher than in the BC@Fe₃O₄@SO₃H, which had a positive effect on strengthening the interaction between the catalyst and polysaccharides in the corncob. However, high concentrations of xylose may accelerate unwanted side reactions, such as consecutive condensation reactions between the furfural and intermediates of the xylose-to-furfural conversion, and thereby result in an unstable furfural yield trend (Dias *et al.* 2006). Additionally, compared with BC@Fe₃O₄@SO₃H, the BC@Fe₃O₄ exhibited a poor corncob conversion activity, with furfural and xylose yields of 38.7 mg/g and 47.6 mg/g, respectively (Table 1, Entry 3), which may have been because of the acidity of the -SO₃H group and the surface modification of the materials with additional oxygenated functional groups during the sulfonation process (Liu *et al.* 2013).

Effect of Warm Water Immersion

During hot water pretreatment, the surface of lignocellulosic biomass becomes rough and hemicelluloses are dissolved and decomposed. These changes are remarkably influenced by the reaction conditions, such as the temperature and pressure. A low temperature and ordinary pressure can alter the biomass morphology, and lead to a minimal dissolution of carbohydrates. Therefore, impregnation with low-temperature water may have an important effect on the successful conversion of lignocellulosic biomass because it can greatly improve the direct contact between the biomass and catalyst (Schneider *et al.* 2016). To further augment the furfural yield and depolymerization of hemicelluloses, the effects of warm water immersion on corncob conversion were examined and the results are shown in Table 2. The ball-milled corncob was first immersed in DI water at a ratio of 1:20 (g/mL) at the desired temperature (40 °C and 60 °C) for 30 min. The HPLC analysis showed that only trace amounts of sugars were dissolved out during the warm water treatment, and the chemical compositions of the treated biomass underwent almost no change. Compared with the non-dipped sample (Table 1, Entry 2), the dissolution and decomposition rates of the corncob hemicelluloses were enhanced after warm water immersion at 40 °C and 60 °C, which may have been because warm water immersion can destroy the complex structure of corncob cell walls, and thus accelerate the dissolution of carbohydrates and improve the interaction between acid catalysts and sugars. This assumption was verified with the SEM images (Fig. 5).

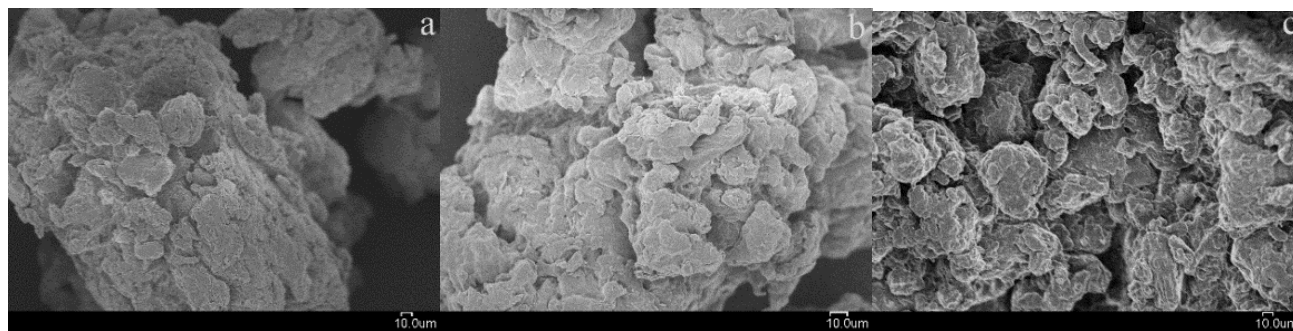


Fig. 5. SEM images of the raw material (a), soaked corncob (40°C) (b), and soaked corncob (60 °C)

Table 2. Product Distribution for the Conversion of Warm Water Immersed Corncob

Sample	Xylose	Glucose	Arabinose	Formic acid	Acetic acid	Furfural	HMF
Soaked corncob (40 °C)	71.6	40.7	10.0	7.8	36.5	54.1	10.8
Soaked corncob (60 °C)	95.4	32.5	14.0	6.5	35.1	49.6	7.8

Values are in mg/g; Reaction conditions: 1.0 g of warm water-immersed corncob, 0.2 g of BC@Fe₃O₄@SO₃H, 20.0 mL of DI water, 180 °C, 30 min, and 300 rpm

The intact plant cell wall of the raw material shows a smooth surface, while the treated samples reveal substantial changes in the surface morphology with a porous property. A much rougher surface could be observed after warm water immersion. However, a slightly lower furfural yield was observed at the relatively high immersion temperature (60 °C), which may have been because of the easier formation of humin at higher xylose concentrations. Based on the higher furfural yield, a water immersion temperature of 40 °C was selected for the subsequent experiments.

Effect of the Reaction Temperature and Time on Corncob Conversion with BC@Fe₃O₄@SO₃H

It was found that the reaction temperature and time had a noticeable influence on the dissolution and depolymerization of corncob polysaccharides. In the present study, a catalytic conversion of warm water-immersed corncob *via* the prepared magnetic solid acid (BC@Fe₃O₄@SO₃H) was performed at 160 °C, 170 °C, and 180 °C for 10 min to 50 min. The main components of the hydrolysates are shown in Table 3.

Table 3. Effect of the Reaction Temperature and Time on the Liquid Composition

Sample (°C-min)	Xylose	Glucose	Arabinose	HMF	Xylooligosaccharides (DP ≤ 6)				
					X2	X3	X4	X5	X6
160-10	13.0	19.5	40.4	1.6	8.3	15.9	23.9	19.3	11.0
160-20	13.2	21.0	34.3	2.0	5.3	15.7	23.1	19.1	10.1
160-30	13.2	21.0	30.7	2.2	4.1	15.4	22.5	13.4	10.0
160-40	13.5	21.5	29.0	2.5	0.0	11.9	18.3	13.0	7.2
160-50	24.4	21.1	25.7	2.8	0.0	10.6	14.3	10.0	6.1
170-10	13.8	24.2	32.2	3.1	0.0	30.4	21.2	15.5	5.4
170-20	15.8	27.4	26.8	3.7	0.0	27.6	19.8	13.2	4.7
170-30	52.4	23.5	19.4	4.7	0.0	21.7	14.7	9.7	4.0
170-40	91.4	22.2	15.4	4.8	0.0	16.1	9.6	9.0	4.1
170-50	87.8	23.9	15.0	5.0	0.0	15.9	10.5	7.0	4.0
180-10	68.4	24.5	18.7	5.7	0.0	19.0	11.8	12.6	4.1
180-20	71.3	28.5	15.1	7.2	0.0	14.2	8.9	9.2	3.4
180-30	71.6	40.7	10.0	10.8	0.0	12.0	7.5	8.7	3.2
180-40	221.6	19.5	4.0	8.6	0.0	10.3	5.4	3.1	2.3
180-50	172.0	18.0	3.1	9.4	0.0	10.5	5.9	2.7	2.7

Values are in mg/g; Reaction conditions: 1.0 g of 40 °C warm water-immersed corncob, 0.2 g of BC@Fe₃O₄@SO₃H, 20.0 mL of DI water, and 300 rpm

Under the tested conditions, the xylose yield progressively increased with an increasing reaction severity (higher reaction temperature or longer reaction time). However, it decreased from 91.4 mg/g to 87.8 mg/g and from 221.6 mg/g to 172.0 mg/g when the reaction time was increased from 40 min to 50 min at 170 °C and 180 °C, respectively. The same tendency was observed in terms of the glucose productivity. Moreover, the glucose yield was higher than the xylose yield under milder conditions, such as 40 min at 160 °C and 20 min at 170 °C. This phenomenon may have been related to the higher glucose content in the raw corncob material. The xylose yield increased noticeably when the reaction time prolonged or reaction temperature was increased, and even exceeded the glucose yield. This result was consistent with the rule that hemicelluloses degrade easier than cellulose (Li *et al.* 2014b), which was also verified by the composition results of the treated corncob, which are given in Table 4. In addition to high xylose productivity, a large amount of glucose was obtained under the investigated conditions, which indicated that the prepared catalysts also showed activity for the conversion of corncob cellulose. The investigation of xylose and glucose productivities during the catalytic conversion process can help us understand the dissolution of corncob polysaccharides and further refine the experiences.

Table 4. Composition of the Treated Corncob under Different Pretreatment Conditions (Relative Weight Percentage)

Sample (°C-min)	Glucose (wt.%)	Xylose (wt.%)	Arabinose (wt.%)	Lignin (wt.%)
160-10	56.5	0.0	1.5	42.0
160-20	53.9	0.0	1.4	44.7
160-30	53.0	0.0	1.7	45.3
160-40	52.2	0.0	1.6	46.2
160-50	51.4	0.0	1.4	47.2
170-10	55.6	0.0	1.1	43.3
170-20	53.0	0.0	1.0	46.0
170-30	53.5	0.0	0.0	46.5
170-40	53.4	0.0	0.0	46.6
170-50	53.3	0.0	0.0	46.7
180-10	53.9	0.0	0.0	46.1
180-20	54.5	0.0	0.0	45.5
180-30	54.7	0.0	0.0	45.3
180-40	54.4	0.0	0.0	45.6
180-50	52.9	0.0	0.0	47.1

Arabinose was another dominating monosaccharide in the corncob hemicelluloses (Li *et al.* 2015b). The arabinose yield decreased with an increasing reaction temperature and time. It was noteworthy that the arabinose productivity was higher than the xylose productivity under mild conditions, which suggested that the hemicellulose side chains degraded faster than the backbone. Up to 96.2% arabinose dissolved from the corncob hemicelluloses during the catalytic hydrolysis process. Although furfural can also be produced from arabinose; the furfural formation rate from arabinose is much slower than from xylose and is even neglected during calculations because of the relatively small amount of arabinose in lignocellulose (Cai *et al.* 2014).

Under acidic conditions, xylose and glucose can be further dehydrated to form furfural and HMF, respectively. Effects of reaction temperature and time on the conversion of 40 °C warm water-immersed corncob are shown in Fig. 6. The highest yields of furfural and HMF were 54.1 mg/g and 10.8 mg/g, respectively, which could be obtained at 180 °C after 30 min. However, a stronger reaction severity may lead to side-reactions that result in further condensation and polymerization of furan compounds into other undesired byproducts, such as soluble polymers and insoluble humin (Weingarten *et al.* 2011). Moreover, the depolymerization and conversion of corncob hemicellulose increased with the increment of reaction temperature and time, indicating that higher reaction rate could be achieved at intensive conditions (Maldonado *et al.* 2014).

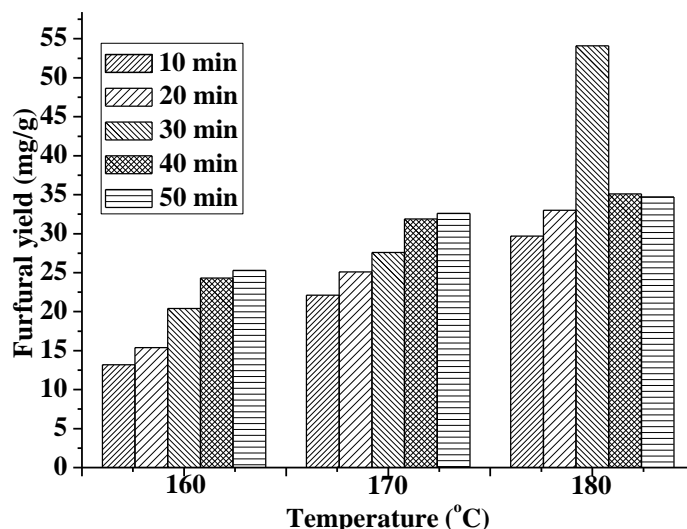


Fig. 6. Furfural yields at different temperatures and time

Reaction conditions: 1.0 g of 40 °C warm water-immersed corncob, 0.2 g of BC@Fe₃O₄@SO₃H, 20.0 mL of DI water, and 300 rpm

Because the vast majority of corncob hemicellulose matter may be released during the solid acid catalytic process, xylose oligomers (XOS) were also considered primary substances in the hydrolysates. In the present study, xylooligosaccharides with a DP less than or equal to 6 in the hydrolysates were detected and these results are shown in Table 3. Under the conditions tested, the XOS amounts (X2, X3, X4, X5, and X6) progressively decreased with the reaction time at various temperatures (160 °C, 170 °C, and 180 °C). The reduction in the xylooligosaccharides yields with the long reaction times was because of the continued hydrolysis of XOS compounds into monosaccharides or oligosaccharides with smaller DP values. Moreover, the total content of the xylo-sugars (xylose and xylooligosaccharides with DP ≤ 6) ranged from 200.0 mg/g to 306.4 mg/g, which indicated that up to 96.1% of the corncob hemicellulose backbone sugars were present as monosaccharides and oligosaccharides in the hydrolysates. Additionally, no xylose was detected in the corncob residues after the catalytic hydrothermal reaction (Table 4), which suggested that almost all of the corncob hemicelluloses dissolved out under the investigated conditions. Due the complexity of the reaction system, the mass transfer should be evaluated in future (Torre *et al.* 2013)

Recycling of the Catalyst

The magnetic property of solid acids is an emerging solution for overcoming separation problems that result from the use of lignocellulosic biomass as the substrate for biofuel and biochemical production. After a heterogeneous reaction, the reaction system contains various components, such as water-soluble products, unreacted substrates, humins, and solid acids. Therefore, determining the recyclability of a catalyst is important to evaluate its efficiency based on economic and environmental factors. In the present study, the prepared BC@Fe₃O₄@SO₃H catalyst was separated from the resulting reaction mixture with an external magnetic field and impregnated with concentrated sulfuric acid again. Its recycled catalytic activities for furfural production are shown in Fig. 7. After three recycle runs, the BC@Fe₃O₄@SO₃H catalyst remained active in the conversion of warm water-immersed corncob into furfural. The small reduction in the furfural yield from 54.1 mg/g (Run 0) to 51.9 mg/g (Run 2) may have been because of the blockage of active acid sites by humin products (Guo *et al.* 2013).

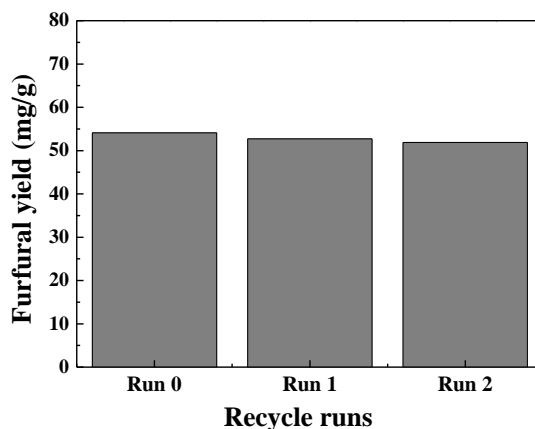


Fig. 7. Recycled catalytic activities of the BC@Fe₃O₄@SO₃H catalyst for furfural production

Follow-up work will be done to optimize the synthesis and pretreatment conditions to improve the catalytic activity of the BC@Fe₃O₄@SO₃H.

CONCLUSIONS

1. The conversion of corncob into furfural was achieved using BC@Fe₃O₄@SO₃H as a catalyst.
2. The prepared catalyst contained -SO₃H, -COOH, and phenolic -OH groups, and the number of H⁺ sites was 1.69 mmol/g.
3. The prepared catalyst exhibited poor adsorption ability for xylose, glucose, and arabinose. Warm water immersion was shown to be an effective approach to destroy the complex structure of the corncob cell walls without sugar leaching.
4. A furfural yield of 54.1 mg/g was obtained at 180 °C after 30 min from 40-°C water-immersed corncob. The recycled catalyst also displayed a high stability after three runs when it was impregnated with concentrated sulfuric acid again.

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