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An efficient magnetic carbon-based solid acid treatment for corncob saccharification with high selectivity for xylose and enhanced enzymatic digestibility†

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An effective method for corncob saccharification was investigated over a magnetic carbon-based solid acid (MMCSA) catalyst in the aqueous phase. MMCSA was synthesized through a simple and inexpensive impregnation–carbonization–sulfonation process. Under the optimal reaction conditions (150 °C, 2 h, 0.5 g corncob, 0.5 g catalyst and 50 ml deionized water), 74.9% of xylose yield was directly obtained from corncob, with 91.7% cellulose retention in the residue. After the reaction, the MMCSA was easily separated from the residue using an external magnet and reused 4 times, showing its high stability and catalytic activity. The enzymatic digestibility of the pretreated residue reached 95.2%, with a total sugar yield of 90.4%. The morphological and structural properties of the natural and treated corncobs were analyzed primarily through 3D X-ray microscopy to characterize the cell wall thickness, porosity, and pore surface area distribution. The increase of macropores (pore surface areas >200 μm²) was beneficial for the accessibility of cellulose to cellulosic enzymes, so the enzymatic digestibility was enhanced immediately. Compared with other traditional hydrolysis methods, this two-step hydrolysis approach represents an environmentally friendly and sustainable saccharification of lignocellulose to produce xylose and glucose while achieving the same level of reaction efficiency.

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1. Introduction

The heavy use of petroleum nowadays has brought about a series of problems such as global warming and energy shortages, so there is sparking interest in the development of various renewable sources for the production of fuels, chemicals and materials.^{1,2} Lignocellulosic biomass as a promising renewable source of energy and organic carbon can be con-

verted to (platform) chemical products and thus has been widely investigated as a replacement for petrochemical products.³

Lignocellulose has a tight structure because of the combined molecular and intramolecular hydrogen bonds among its three major components (hemicellulose, cellulose and lignin). For the valorization of lignocellulose towards highly value-added chemicals, it is necessary to deconstruct its structure and subsequently degrade each component. As a typical example, saccharification of lignocellulose followed by sugar fermentation to produce bioethanol as a promising fuel represents one of the most important pathways for the utilization of lignocellulose. Hence, the development of environmentally friendly and effective methods for lignocellulose saccharification has been viewed as one of the main research focuses in the field of lignocellulose utilization.

Enzymatic hydrolysis is viewed as a mild route for lignocellulose saccharification and the enzymatic digestibility is greatly influenced by the lignocellulose pretreatment efficiency. Various pretreatment methods, including physical, chemical, physicochemical and biological methods, have been applied to promote lignocellulose enzymatic digestibility.^{4–6}

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Ball milling is a common physical pretreatment method for lignocellulose. Ursula *et al.*⁷ pretreated cellulosic materials using ball milling and found that under the same enzymatic digestibility, the dosage of enzyme was lower than in the case of the untreated material, indicating that ball milling could improve enzymatic hydrolysis efficiency. But this method requires high energy consumption, limiting its large-scale application.

A combined technique of alcohol-based organosolv treatment and ball milling has been shown as an effective physicochemical pretreatment method. Hiden *et al.*⁸ used a mixture of ethanol, ethylene glycol, water and acetic acid as the solvent and combined short-time ball milling to treat Japanese cypress. The results showed that the enzymatic digestibility of Japanese cypress was greatly improved after this physicochemical pretreatment. But the process posed disadvantages that the reducing sugar obtained was soluble in liquid (which was difficult to separate), and the acidic alcohol-based organosolv treatment often led to equipment corrosion.

Biological pretreatment has also been applied to pretreat lignocellulose, which can degrade the lignin component in lignocellulose and loosen the structure. Zhao *et al.*⁹ pretreated cornstalk with *Phanerochaete chrysosporium* to enhance enzymatic saccharification. The maximum enzymatic digestibility was found to be 47.3% after 15 days, which was 20.3% higher than that found in the control experiments without pretreatment. Although biological technologies are considered the least expensive among the existing pretreatment technologies (because they consume little energy and do not require chemical supplements), such processes need constant attention for the proper growth of microorganisms and the hydrolysis rate enhancement associated with biological pretreatment is quite low.

Chemical pretreatment using mostly liquid acids and alkaline materials has been the most commonly used method. Kim *et al.*¹⁰ reported that corn stover digestibility could reach 92.5% with 10 FPU g⁻¹ of glucan after 90 min of aqueous ammonia pretreatment (here, FPU is the abbreviation of filter-paper units; one unit of FPU is defined as the amount of cellulase required for producing 1 μ mol reducing sugars per minute). This result indicates that alkali pretreatment could improve the enzymatic digestibility. However, this process requires a large amount of alkaline materials to destroy the lignin structure in lignocellulose and produces black liquor in a significant amount, which has limited its large-scale utilization. Liquid acid pretreatment is another effective method. The acid can remove the hemicellulose in the lignocellulose, and increase the accessibility between enzymes and the substrate to improve the enzymatic digestibility. Amnuaycheewa *et al.*¹¹ pretreated rice straw with oxalic acid, and the pretreatment enhanced the enzymatic saccharification up to about 213 mg of glucose yield from 500 mg of the pretreated sample (*i.e.*, the enzymatic digestibility was almost 42.6%), which is 2.7 times higher than that obtained from the untreated rice straw. The disadvantage of this pretreatment

method is that liquid acids are toxic and can cause environmental pollution and equipment corrosion.¹² Yet, this is the only technology with promising commercial application prospects.

Lignocellulose pretreatment using solid acid catalysts presents some advantages over the methods mentioned above, which include among others good catalytic efficiency similar to that of liquid acids, easy catalyst separation and reusability. In recent years, solid acid catalysts, including zeolites,¹³ Nafion,¹⁴ Amberlyst-15,¹⁵ SBA-15,¹⁶ and carbon-based solid acids, have been used for the hydrolysis of lignocellulose. Among these solid acids, carbon-based solid acids have shown higher catalytic activity, water thermal stability and reusability than other solid acid catalysts in lignocellulose hydrolysis.¹⁷ Li *et al.*¹⁸ synthesized amorphous carbon-bearing -SO₃H, -COOH, and -OH groups and used them in the hydrolysis of corncob, obtaining the highest 82.5% yield of xylose, a result that was attributed to the ability of the carbon material to adsorb and break the β -1,4 glucan bond to release saccharides. But a disadvantage noticed in this process is that the carbon-based solid catalyst was hard to separate from the residue after the hydrolysis reaction. A magnetic carbon-based solid catalyst which can be separated easily using an external magnet is thus a good choice. Ansanay *et al.*¹⁹ reported that a series of magnetic sulfonic acid solids synthesized from activated carbon and *p*-toluene sulfonic acid could be used to pretreat switchgrass, miscanthus and triticale hay, in order to remove the hemicellulose of raw plant materials and increase its enzymatic digestibility. The enzymatic digestibility was found to be indeed improved compared to that of the raw plant material, indicating that a magnetic carbon-based solid acid could be used as a pretreatment reagent. However, the enzymatic digestibility of the pretreated biomass was still around 60% (a result lower than that found in other pretreatment methods), indicating that the prepared solid acid catalysts were not active enough in loosening the structure of lignocellulose in order to provide sufficient accessibility for cellulose to cellulase enzymes. Thus, there is a long way to go before this kind of magnetic carbon-based solid acid pretreatment can be commercially applied.

In this work, we have reported on the preparation of a novel magnetic carbon-based acid synthesized from a model compound of cellulose through an impregnation-carbonization-sulfonation process and its utilization in the pretreatment of corncob (a typical and abundant waste of agricultural production that draws attention as a raw material for producing bioethanol). This carbon-based acid not only showed high catalytic activity and selectivity for xylose in the pretreatment of corncob, but also significantly improved the enzymatic digestibility of the pretreated corncob residue to a much higher level than that obtained with the raw plant material. Furthermore, the catalyst could be easily separated out with an external magnet and reused multiple times with only a slight decline in its catalytic ability. This two-step hydrolysis process proved to be a more sustainable and effective method for treating lignocellulose to produce reducing sugars.

2. Experimental

2.1 Materials

Corncob powder (60–80 mesh) was obtained from the Shandong province of China, and oven-dried at 80 °C to a constant weight. Microcrystalline cellulose (GR), sulfuric acid (98%, GR) and anhydrous ferric chloride were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Cellulase (190 FPU g⁻¹) was obtained from Imperial Jade Biotechnology Co., Ltd (Ningxia, China).

2.2 Catalyst preparation

10 g microcrystalline cellulose (≤ 120 meshes) was added to 1000 mL of FeCl₃ solution with a concentration of 10 mmol L⁻¹, and the mixture was stirred at 400 rpm for 5 h. Then, water in the mixture was evaporated at 100 °C, and the remaining mixture was dried in a vacuum oven at 105 °C overnight to obtain the impregnated microcrystalline cellulose with a Fe content of approximately 1 mmol g⁻¹.

Subsequently, the Fe-impregnated microcrystalline cellulose was carbonized at 250 to 450 °C in a tube furnace under a N₂ atmosphere for 1 to 5 h to produce a magnetic microcrystalline cellulose-derived carbon (MMC) base. The thus obtained MMC solid was then sulfonated at 110 to 150 °C with sulfuric acid (98% (w/w%); the ratio of solid to liquid = 1 : 10 (g : mL)) for 11 to 15 h to introduce -SO₃H groups. The sulfonated magnetic carbon material was recovered through filtration and washed with hot water (>80 °C) until no SO₄²⁻ ion was detected using BaCl₂ solution, and it was then dried at 105 °C overnight. The thus prepared solid acid was labeled as MMCSA.

2.3 Corncob hydrolysis *via* solid acid pretreatment

For optimizing MMCSA catalyst preparation. The hydrolysis reaction, using the carbon-based solid acid catalyst MMCSA (1.0 g; prepared under different conditions as detailed in section 2.2), corncob (0.5 g) and deionized water (50 mL), was carried out in a 100 mL thick-walled pressure bottle (Beijing Synthware Glass Co., Ltd, China) with a 2 cm magnetic bar attached to a magnetic stirrer in a 120 °C oil bath for 10 h. After the reaction, the supernatant was collected for further analysis (*cf.* section 2.6).

For the test of catalyst reusability. The catalyst was separated out of the reaction medium with an external magnet, then washed and dried in an oven at 105 °C until it reached a constant weight to be ready for the next use. The prepared optimized catalyst was reused four times for the hydrolysis reaction under the same hydrolysis reaction conditions as shown above.

Optimization of corncob pretreatment conditions. A mixture of corncob, water, and the optimized catalyst was placed in an autoclave. Hydrolysis was carried out in various ranges of reaction temperature (130–170 °C), reaction time (0.5–6 h), catalyst dosage (0–1.0 g) and corncob dosage (0.125–1.0 g). After the reaction, the supernatant was collected to analyze the products (see section 2.6). The catalyst was separated out from the reaction medium with an external magnetic field for reuse. The

corncob residue was then dried in a vacuum oven at 50 °C to a constant weight for use in the enzymatic hydrolysis.

2.4 Enzymatic hydrolysis of the pretreated corncob residue

0.1 g of corncob residue (collected from multiple runs with solid acid pretreatment under the optimum reaction conditions) was hydrolyzed at 50 °C for 1 to 96 h in a 5 mL centrifuge tube with an agitation speed of 150 rpm on a rotary shake. The substrate concentration was 5% (w/v) with cellulase at a loading of 20 FPU g⁻¹ and 40 FPU g⁻¹ for the dry solid. The hydrolysate was collected for product analysis.

2.5 Characterization of catalyst, corncob and hydrolyzed residue

A pattern of Fourier transform infrared (FT-IR) spectroscopy for the prepared catalyst was analyzed using a TENSOR 27 spectrometer (Bruker, Karlsruhe, Germany) through the standard KBr pellet method within the range of 400 to 4000 cm⁻¹. X-ray photoelectron spectroscopy (XPS) of the catalyst was performed on an ESCALAB 250Xi (Thermo, Waltham, USA). Binding energy was calibrated with C 1s at 284.8 eV. X-ray diffraction (XRD) was performed on an X'PertPro MPD (PANalytic, Almere, the Netherlands) operating at 40 kV and 40 mA using a CuK α radiation source within the 2 θ range from 5° to 80° at a scanning step length of 4° min⁻¹. The catalyst morphologies were determined with a transmission electron microscope (TEM; Hitachi HT7700, Tokyo, Japan) with a working voltage of 20.0 kV.

The number of functional groups within the catalyst was characterized *via* elemental analysis (Vario EL cube, Elementar, Frankfurt, Germany) and cation-exchange analysis. The literature has shown *via* X-ray photoelectron spectroscopy (XPS) analysis that all the sulfur in the carbon materials was expected to be confined to -SO₃H groups, thus the densities of -SO₃H groups were estimated based on the sulfur content as can be inferred from sample compositions determined *via* elemental analysis.²⁰ The total contents of the (-SO₃H + -COOH) functional groups and (-SO₃H + -COOH + -OH) functional groups were estimated from the exchange of Na⁺ in the aqueous NaCl and NaOH solutions, respectively, in order to further determine the proportion of each functional group.¹⁸ The strength of the acid sites within the catalyst was tested using the Hammett method.²¹

The surface morphologies of the raw and pretreated corncob were characterized using scanning electron microscopy (SEM, S-4800, Hitachi, Tokyo, Japan). Magnetic properties of the catalyst were examined using a vibrating sample magnetometer (VSM; 7410, Lake Shore Company, Colchester, USA) for the sample particle hysteresis regression curve and Ms (saturated magnetization) with an absolute accuracy of better than 2%. The raw and pretreated corncob were studied using a 3D X-ray microscope (Nanovox-2100, Sanying Precision Engineering Research Center, China); photographs were taken at 41 kV and 220 μ A, and the resolution of the measurement was set to 1 $\times$ 1 $\times$ 1 μ m.

2.6 Analytical procedure

The concentrations of xylose, glucose, arabinose, and byproducts (furfural, 5-hydroxymethyl furfural, acetic acid, formic acid, and D-glucuronic acid) in the hydrolysate were analyzed by high-performance liquid chromatography (Waters 2695, Milford, USA; Shodex sugar SH-1011 chromatographic column, mobile phase of 5 mM H₂SO₄, at a flow rate of 0.5 mL min⁻¹, column temperature at 50 °C). The sugar oligomers were measured according to the method in the literature.²²

The components of the raw and pretreated corncob were analyzed by the NREL standard analytical method.²² The results revealed that the corncob was composed of 35.9% glucan, 34.1% xylan, 3.5% arabinose, and 22.0% lignin, all expressed on a dry-weight basis.

2.7 Calculation equations

The yields of sugars (xylose, glucose, and arabinose) were defined as

$$\text{Sugaryield} = \frac{N}{M} \times 100\% \quad (1)$$

where N is the mole number of sugar in the hydrolysate and M is the mole number of sugar in the raw corncob.

The enzymatic digestibility of the raw or pretreated corncob was defined as

$$\text{Enzymatic digestibility} = \frac{n}{m} \times 100\% \quad (2)$$

where n is the mole number of glucose in the enzymatic hydrolysate and m is the mole number of glucose in the raw or pretreated corncob.

The total sugar yield in the process of corncob pretreatment followed by the enzymatic hydrolysis was obtained from

$$\text{Total sugar yield} = \frac{a \times b \times c + a \times d \times e + f \times g \times h + f \times i \times j}{a \times b + a \times d} \times 100\% \quad (3)$$

where a is the mass quantity of corncob; b is the proportion of xylan in the corncob; c is the yield of xylose in the pretreatment process; d is the proportion of glucan in the corncob; e is the yield of glucose in the pretreatment process; f is the mass quantity of the corncob hydrolysis residue; g is the proportion of xylan in the corncob hydrolysis residue; h is the yield of xylose in the enzymatic process; i is the proportion of glucan in the corncob hydrolysis residue; and j is the yield of glucose in the enzymatic process.

3. Results and discussion

3.1 Optimization of MMCSA preparation

A series of magnetic carbon-based solid catalysts were prepared through the impregnation–carbonization–sulfonation method and tested in corncob hydrolysis. The influence of various catalyst preparation parameters on the hydrolysis

results and the total acid amount in the catalyst are presented in Fig. 1. Fig. 1(a) presents the impact of the carbonization temperature. The catalyst was synthesized at different carbonization temperatures varying from 250 to 450 °C for 3 h and then sulfonated at 150 °C for 10 h. It was found that the total acid amount of the catalyst first increased and then decreased over this temperature range, and the yields of xylose, arabinose, and glucose had the same trend. When the carbonization temperature was lower, amorphous carbon consisting of small and flexible polycyclic aromatic carbon sheets was formed and only to the edges of these carbon sheets were the –SO₃H groups attached.²⁰ As the temperature was increased, the formation of an amorphous carbon sheet was more favored and the acidic functional group was more easily loaded onto the carbon skeleton.²⁰ However, a too high temperature level would first cause the –OH and –COOH functional groups on the catalyst surface to fall off, thus contributing to the total acid amount decrease and making it unfavorable for hydrolysis.²³ Meanwhile, the increasing carbonization temperature made the formed amorphous carbon harder since the flexibility of polycyclic aromatic carbon was decreased due to the plane growth and the stacking of the carbon sheets. The latter would thus contribute to the sulfonic acid amount decrease as well. It should be noted that although such large and inflexible amorphous aromatic carbon could still be sulfonated, it was more difficult for the reactant to reach the –SO₃H group in the bulk, which tended to yield a limited catalytic activity as well.²⁰ Thus, it was observed in the current work that a carbonization temperature of *ca.* 300 °C led to the highest total acid amount and the best xylose yield.

However, it was found through external magnet testing that the catalysts obtained by carbonation at temperatures of 250 and 300 °C were not magnetic. This is possible due to the fact that at such relatively low temperature levels, few reducing reactants were generated during the carbonization process and thus the quantity of Fe₃O₄ formed was not enough (see section 3.2 for more details on the reactions related to Fe₃O₄ formation during MMCSA synthesis). In this work, the carbonation process is similar to the torrefaction process of biomass pyrolysis. Zhang *et al.*²⁴ reported that there was only 1.63% of CO at 290 °C, which was driven from hemicellulose, in the noncondensable gas and the generation of H₂ and C needs a higher torrefaction temperature than that of CO. Meanwhile, the necessary torrefaction temperature of cellulose is higher than that of hemicellulose. For example, it has been shown that hemicellulose decomposed at a temperature in the range of 225–325 °C, and cellulose at 305–375 °C as Wei-Hsin Chen *et al.* reported.²⁵ For the microcrystalline cellulose used in this work, an even slightly higher torrefaction temperature might be needed, given its tighter structure than cellulose in biomass. Therefore, there were few reducing reactants produced at a temperature below *ca.* 300 °C, and as a result, there were not enough Fe₃O₄ particles formed to maintain magnetism. Thus, 350 °C was selected as the optimal carbonization temperature for the magnetic catalyst based on the highest xylose yield and the total acid amount obtained within the temperature range of 350 to 450 °C.

Fig. 1 Effects of carbonization temperature (a), carbonization time (b), sulfonation temperature (c) and sulfonation time (d) on the catalytic activity in corncob hydrolysis and the total amount of acid in the catalyst. In (a) and (b), the sulfonation reaction conditions were fixed at 150 °C for 10 h. Hydrolysis reaction conditions: 120 °C, 10 h, 1.0 g of catalyst, 0.5 g of corncob and 50 ml deionized water.

As shown in Fig. 1(b), when the carbonization time was increased from 1 to 5 h (at a fixed carbonization temperature of 350 °C), the total amount of acid produced remained nearly the same, and the yields of xylose, arabinose and glucose changed little. This indicates that the carbonization time had no significant impact on the catalytic activity of the MMCSA. The best xylose yield was achieved with 1 h of carbonization. It is thus possible that the carbonization temperature is the most important factor for the determination of the carbon structure of the catalyst during the carbonization process. Therefore, at the optimized carbonization temperature of 350 °C, the desired structure of carbon (containing small and flexible polycyclic aromatic carbon sheets) essential for good acid group attachment and catalytic activity was already formed after *ca.* 1 h of carbonization treatment and remained stable. Therefore, the effect of further prolonging the carbonization time is not obvious.²⁶

The impact of the catalyst sulfonation temperature on the catalytic activity is shown in Fig. 1(c). The catalyst was sulfo-

nated at different temperatures varying from 110 to 150 °C for 10 h after the catalyst was carbonized at 350 °C for 1 h. When the sulfonation temperature was increased from 110 to 130 °C, the total acid amount and the yields of xylose, arabinose, and glucose all increased, indicating that an increase in the sulfonation temperature led to a faster sulfonation reaction rate and thus might be favorable to the linking of aromatic carbon rings with the sulfonic acid groups.²⁷ However, when the sulfonation temperature was increased further to 150 °C, the total acid amount and the yields of xylose, arabinose and glucose all decreased, indicating that a further increase in the sulfonation temperature could lead to a more significant structure damage and dehydration of the catalyst by highly concentrated sulfuric acid (98%, w/w%) used.²⁸ Meanwhile, another reason for the decreased total acid amount could be that the desulfonation reaction was more favored at high temperatures.²⁹

The impact of catalyst sulfonation time is shown in Fig. 1(d). The catalyst was sulfonated at 130 °C for different

durations, varying from 6 to 14 h. When the sulfonation time was increased from 6 to 10 h, the total acid amount of the catalysts and the yields of xylose, arabinose, and glucose all increased, indicating that the sulfonation reaction has not reached equilibrium yet and thus the increase in the sulfonation time has increased the acid functional groups of the catalyst.²⁷ When the sulfonation time was further increased to 14 h, the total acid amount and the yields of xylose, arabinose and glucose all decreased. This decrease could be due to the fact that an increase in the sulfonation time has reduced the amount of hydroxyl and carboxyl groups and resulted in a weak attraction between the catalyst and corncob.³⁰ The sulfuric acid used for sulfonation is actually a dehydrating agent, and would result in the hastening of the complete carbonization process, whereby it removed the inherent hydrogen and oxygen groups present along with the attachment of sulfonic acid groups to the carbon backbone. Thus, a long period of sulfonation could induce the removal of -OH and -COOH acid groups, and cause a decrease in the total acid amount.²⁶

From the above analysis, the optimal carbonization and sulfonation conditions for the preparation of MMCSA were identified as 350 °C for 1 h and 130 °C for 10 h, respectively.

As shown in Fig. 1, the yields of monosaccharides were consistent with the total acid amount of the catalyst synthesized under different conditions, especially regarding xylose and arabinose. However, the yield of polysaccharides varied opposite to the changes in the total acid amount, showing that a high total acid amount in the catalyst could promote the hydrolysis of hemicellulose and polysaccharides into monosaccharides. Meanwhile, the concentrations of byproducts (furfural, formic acid, acetic acid, and D-glucuronic acid) in the hydrolysate were extremely low (less than 0.4 g L⁻¹), as shown in Fig. S1,† indicating that few of the saccharides were degraded into the corresponding byproducts and thus the catalyst had a high selectivity for monosaccharides.

3.2 Characterization of MMC and the optimized MMCSA

The reactions during the MMC synthesis process are shown in eqn (4)–(8).³¹ Fe pre-impregnated into the microcrystalline cellulose in the form of FeCl₃ was first hydrolyzed into FeO(OH) in the evaporation process, and then the Fe-impregnated microcrystalline cellulose was converted into MMC *via* the carbonization process. In this process, FeO(OH) was reduced into Fe₃O₄ by components such as hydrogen (H₂), carbon monoxide (CO) and amorphous carbon (C), which were all formed in the carbonization process.

After the sulfonation of MMC, the MMCSA was prepared and the samples' magnetic and recoverable properties were characterized by XRD, TEM, XPS and VSM.

As Fig. S2† shows, the XRD patterns of the MMC and MMCSA both exhibited broad and weak diffraction peaks at $2\theta = 20\text{--}30^\circ$, which can be attributed to the amorphous carbon containing aromatic carbon sheets in a considerably random fashion.³² The diffraction peaks at $2\theta = 30.1^\circ$, 35.4° , 43.1° , 56.9° and 62.5° were assigned to the (2 2 0), (3 1 1), (4 0 0), (5 1 1) and (4 4 0) lattice planes of Fe₃O₄ according to the standard magnetite crystal structure data (JCPDS card no. 19-0629). The XRD results indicated that both MMC and MMCSA showed magnetic performance due to the enclosed Fe₃O₄.³³ The TEM images (Fig. S3†) further confirmed that Fe₃O₄ nanoparticles were dispersed in the MMCSA.

The separation and recovery of solid catalysts is an important factor for practical application.³⁴ The magnetic hysteresis curves of the samples showed nonlinear and reversible behavior, with superparamagnetism (Fig. S4†). The saturation magnetization intensity value of MMCSA is 6.7 Am² kg⁻¹, which is sufficient for the separation of the particles by an external magnetic field, freeing them for reuse. After the pretreatment of corncob, the separation ability of MMCSA from the reactant was tested, as Fig. 2 shows. MMCSA was well separated from the corncob residue with an external magnet.

3.3 Acidic group analysis of the optimized MMCSA

In order to understand the acidic groups in the MMCSA, it was characterized by FT-IR, elemental analysis, acid-base titration and the Hammett method.²¹

From the FT-IR spectra (Fig. S5†), it was found that peaks at around 1035 and 1181 cm⁻¹ could be ascribed to the O=S=O stretching vibration in -SO₃H, indicating that -SO₃H was successfully introduced to the carbon material.³⁵ The peak at around 1694 cm⁻¹ could be attributed to the C=O bending vibration in -COOH³⁶ and the peak at around 3311 cm⁻¹ to the O-H stretching vibration in -COOH and phenolic -OH.¹⁸

Fig. 2 Separation of the catalyst from the mixed reaction system.

The peak at around 1580 cm^{-1} was clearly due to the C=C stretching vibration in aromatic carbons.³⁷ The peaks at 635 cm^{-1} could be assigned to an Fe–O stretching vibration in the Fe_3O_4 component and the one at 809 cm^{-1} was due to the C–O–S stretching vibration.²⁷ These observations indicate that MMCSA posed $-\text{SO}_3\text{H}$, $-\text{COOH}$, and $-\text{OH}$ groups generated in the processes of carbonization and sulfonation.¹⁸

The XPS spectra of MMC and MMCSA are shown in Fig. S6.† In the XPS curve of MMCSA, the single peak observed at 168 eV was ascribed to S 2p of $-\text{SO}_3\text{H}$, indicating that all the S atoms in the MMCSA were present only in the form of $-\text{SO}_3\text{H}$. The XPS result confirmed that $-\text{SO}_3\text{H}$ was successfully introduced to the carbon skeleton during the sulfonation process.³⁸

Elemental analysis and a cation-exchange experiment revealed that the MMCSA composition was $\text{C}_{0.505}\text{H}_{0.3014}\text{O}_{0.933}\text{S}_{0.085}\text{Fe}_{0.322}$ and that the amounts of $-\text{SO}_3\text{H}$, $-\text{COOH}$ and phenolic $-\text{OH}$ groups bonded to the graphene were 0.85, 0.55 and 1.42 mmol g^{-1} , respectively. The acid strength of the catalyst ranged from -8.20 to -11.35 .

On the basis of these characterization results, the schematic carbon structure was proposed as shown in Fig. 3. The prepared material is amorphous carbon consisting of $-\text{SO}_3\text{H}$, $-\text{COOH}$ and phenolic $-\text{OH}$ groups bearing nanographene sheets in a considerably random fashion. If a carbon material is composed of uniform functionalized graphene sheets, each graphene sheet is expected to bind $-\text{SO}_3\text{H}$ and phenolic $-\text{OH}$. The carbon material possesses a high density of almost neutral phenolic $-\text{OH}$ in addition to Brønsted acid sites ($-\text{SO}_3\text{H}$ and $-\text{COOH}$). This is distinct from conventional solid acids with single functional groups. These different functional groups present in the MMCSA played different roles, but there was also a synergistic effect between them in terms of promoting the hydrolysis reaction. The efficient conversion of hemicellulose in corncob requires a strong interaction between the carbon-based solid acid and corncob which could make the Brønsted acid sites ($-\text{SO}_3\text{H}$ and $-\text{COOH}$) approach the corncob surface effectively and then attack the β -1,4-glycosidic bond to release saccharides. The phenolic $-\text{OH}$ which could form strong hydrogen bonds with oxygen atoms in the β -1,4-glycosidic bond acted as the linkage between the carbon-based solid acid and corncob.³⁹ Besides, Li *et al.*¹⁸ employed hydrogen peroxide to enhance the acidity of the prepared sodium lignosulfonate-derived carbon-based catalyst (SI-C-S) which

already contained $-\text{SO}_3\text{H}$, $-\text{COOH}$ and $-\text{OH}$. They found that such treatment introduced more weakly acidic groups ($-\text{COOH}$ and $-\text{OH}$) instead of $-\text{SO}_3\text{H}$, and these introduced $-\text{COOH}$ and $-\text{OH}$ groups were also found to improve the xylose selectivity significantly.

3.4 Reusability of MMCSA

Long-term stability is an important property of solid acid catalysts for their potential use in biomass pretreatment. After corncob hydrolysis, MMCSA was separated from the corncob residue using an external magnet, and the collected MMCSA was reused as a catalyst in the following hydrolysis. After five reuse cycles, the xylose yield decreased gradually from 70.8% to 62.9% (Fig. 4), indicating that the catalyst still showed a high catalytic activity.

The element content of the reused catalysts was analyzed and is shown in Table 1. The composition of MMCSA was $\text{C}_{5.105}\text{H}_{3.014}\text{O}_{0.933}\text{S}_{0.085}\text{Fe}_{0.322}$ at the beginning and $\text{C}_{5.028}\text{H}_{2.996}\text{O}_{1.007}\text{S}_{0.077}\text{Fe}_{0.322}$ after the last use, and the proportions of C, H, Fe, O and S did not significantly change after each reuse, indicating that the catalyst had high stability in this reaction system. The slightly decreased total acid amount

Fig. 4 Reusability of the optimized MMCSA in corncob pretreatment. Hydrolysis reaction conditions: $120\text{ }^{\circ}\text{C}$, 10 h, 0.5 g corncob, 1.0 g catalyst and 50 ml deionized water.

Fig. 3 Schematic illustration of the preparation, acidic groups and structure of MMCSA. The schematic diagram does not represent the real amount and distribution of functional groups.

Table 1 Composition and amount of $-\text{SO}_3\text{H}$ in the optimized MMCSA over multiple recycle tests

	Fe	C	H	S	O		
Reuse no.	%					Chemical formula	$-\text{SO}_3\text{H}$ (mmol g^{-1})
1	18.054	61.270	3.014	2.727	14.935	$\text{C}_{5.105}\text{H}_{3.014}\text{O}_{0.933}\text{S}_{0.085}\text{Fe}_{0.322}$	0.850
2	17.988	60.933	2.988	2.689	15.402	$\text{C}_{5.077}\text{H}_{2.988}\text{O}_{0.962}\text{S}_{0.084}\text{Fe}_{0.321}$	0.840
3	18.121	59.899	3.045	2.531	16.404	$\text{C}_{4.991}\text{H}_{3.045}\text{O}_{1.025}\text{S}_{0.079}\text{Fe}_{0.323}$	0.790
4	18.252	61.227	3.077	2.501	14.943	$\text{C}_{5.102}\text{H}_{3.077}\text{O}_{0.933}\text{S}_{0.078}\text{Fe}_{0.325}$	0.780
5	18.063	60.338	2.996	2.486	16.117	$\text{C}_{5.028}\text{H}_{2.996}\text{O}_{1.007}\text{S}_{0.077}\text{Fe}_{0.322}$	0.770

and $-\text{SO}_3\text{H}$ amount of the catalysts may be the cause of the declining catalytic activity.

From Fig. 4, it was found that the total amount of acid decreased from 2.82 mmol g^{-1} to 2.01 mmol g^{-1} after 5 reuses, with a decline rate of 28.72%. From Table 1, the amount of $-\text{SO}_3\text{H}$ decreased from 0.85 mmol g^{-1} to 0.77 mmol g^{-1} (*i.e.*, with a total of 9.4% decrease over 5 reuses). Thus, the hydro-

lytic desulfonation during corncob pretreatment occurred only slightly. This result was qualitatively in accordance with the previous research of Asakura *et al.*²⁹ They reported that the $-\text{SO}_3\text{H}$ group on sulfonic acid cation exchange resins was thermally stable in the aqueous phase up to 120 °C. Though the desulfonation was weak in the current work, the decrease of the total amount of acid was more obvious (*i.e.*, with a

Fig. 5 Effect of hydrolysis temperature (a), hydrolysis time (b), catalyst dosage (c), and corncob dosage (d) on sugar yields from corncob pretreatment catalyzed by the optimized MMCSA. In (a)–(d), only one hydrolysis parameter was varied, and the others remained the same as in the standard procedure.

decrease of 0.81 mmol g^{-1} over 5 reuses; cf. Fig. 4). Thus, the removal of $-\text{COOH}$ or phenolic $-\text{OH}$ occurred during the pretreatment. As mentioned before, the amounts of $-\text{SO}_3\text{H}$, $-\text{COOH}$, and phenolic $-\text{OH}$ groups bonded to the optimized MMCSA prior to the pretreatment reaction test were 0.85 , 0.55 and 1.42 mmol g^{-1} , respectively. It can be predicted accordingly that the removal of the phenolic $-\text{OH}$ group was more responsible for the total acid amount decrease over multiple reuses. However, Fig. 4 also reveals that the decrease in the xylose yield was only slightly significant, indicating that the catalytic activity of MMCSA was still high after 4 times of reuse. A possible reason here is that although some phenolic $-\text{OH}$ groups had been removed, the synergetic effect between different acid functional groups was still largely present to maintain a high catalytic activity in xylose production.

3.5 Corncob pretreatment catalyzed by MMCSA

To obtain a high xylose yield for further enzymatic hydrolysis, the pretreatment conditions (including hydrolysis temperature, hydrolysis time, catalyst loading and corncob dosage) were optimized, as shown in Fig. 5. The reaction was first conducted at temperatures ranging from 130 to 170°C with 0.5 g of catalyst, 0.5 g of corncob and 50 ml of deionized water, the results of which are shown in Fig. 5a. When the pretreatment temperature was increased from 130 to 150°C , the xylose yield increased from 59.3% to 67.7% . However, when the temperature was further increased to 170°C , the xylose yield decreased dramatically to 15.3% . These results imply that a temperature increase could promote both the reaction rate of the corncob hydrolysis and xylose degradation, but a relatively lower reaction temperature (up to *ca.* 150°C) is favorable for hemicellulose hydrolysis due to its higher reaction rate than that of xylose degradation, thus increasing the xylose yield. Above 150°C , the xylose degradation reaction rate tended to be much faster than the hemicellulose hydrolysis rate, leading to a xylose yield decrease.⁴⁰

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Fig. 5b shows the influence of the pretreatment reaction time on the catalytic activity. The reaction was performed from 0.5 to 6 h , at 150°C with 0.5 g of catalyst, 0.5 g of corncob, and 50 ml deionized water. When the reaction time was increased from 0.5 to 2 h , the xylose yield increased from 49.2% to 73.4% . When the reaction time was further increased to 6 h , the xylose yield decreased slightly to 67.7% . This implies that along with corncob hydrolysis to produce xylose, xylose was degraded more significantly at a longer reaction time due to its concentration build up in the reaction system. Thus, an optimum reaction time (*ca.* 2 h) existed for obtaining the highest xylose yield.

Fig. 5c presents the effect of the catalyst loading on the catalytic activity. The catalyst amount was investigated from 0 to 1.0 g at 150°C for 2 h with 0.5 g of corncob and 50 ml of deionized water. When the catalyst loading was increased from 0 to 0.5 g , the xylose yield increased from 2.8% to 73.4% . The xylose yield was very low in the absence of the catalyst, indicating a negligible degradation of the hemicellulose fraction of corncob under the reaction conditions, thus the use of a cata-

Table 2 Catalytic activity comparison of MMCSA and other catalysts in corncob hydrolysis

Catalyst	Xylose yield (%)	Glucose yield (%)
^a Amberlyst-15 ⁴¹	60.2	5.8
^a HZSM-5 ⁴¹	11.4	5.7
^a Gp- SO_3H - H_2O_2 ⁴¹	78.4	6.1
^b $\text{Fe}_3\text{O}_4/\text{C}-\text{SO}_3\text{H}$ ²⁷	44.3	—
^c $\text{C}-\text{SO}_3\text{H}$ ⁴²	78.1	7.4
^d MMCSA ^{This work}	74.9	7.6

^a Catalyst, 0.5 g ; corncob 0.25 g ; water, 25 ml ; 140°C , 12 h . ^b Catalyst, 1.0 g ; corncob 0.5 g ; water, 50 ml ; 160°C , 16 h . ^c Catalyst, 0.25 g ; corncob 0.25 g ; water, 25 ml ; 140°C , 6 h . ^d Catalyst, 0.5 g ; corncob 0.5 g ; water, 50 ml ; 150°C , 2 h .

Fig. 6 Enzymatic digestibility of corncob before and after the pretreatment. Pretreatment conditions: 150°C , 2 h , 0.5 g of corncob, 0.5 g of the optimized MMCSA catalyst, and 50 mL of deionized water. Enzymatic digestion conditions: 5% substrate concentration (*w/v*), 50°C .

Table 3 Compositions of the corncob and residue after pretreatment

	Contents (%)			Removal rates (%)		
	Xylan	Glucan	Lignin	Hemicellulose	Cellulose	Lignin
Raw	34.1	35.9	22.0	87.0	8.3	44.6
Pretreated	8.6	63.6	23.5			

Pretreatment conditions: 150°C , 2 h , 0.5 g of corncob, 0.5 g of the optimized MMCSA catalyst, and 50 mL of deionized water.

lyst is essential. When the catalyst loading was further increased to 1.0 g, the xylose yield decreased to 65.7%, possibly because of the presence of sufficient acid sites for driving undesired side reactions when the catalyst was overused. The optimal catalyst loading was hence found to be *ca.* 0.5 g.

The effect of corncob dosage was investigated as well (varied from 0.125 to 1.0 g; tested at 150 °C for 2 h with 0.5 g of catalyst and 50 ml of deionized water). When the corncob dosage was increased from 0.125 to 0.5 g, the xylose yield

increased from 50.0% to 73.4%. When the corncob dosage was further increased to 1.0 g, the xylose yield decreased slightly to 69.4%, showing that a low liquid-to-solid ratio is detrimental to mass transfer (*i.e.*, hindering an efficient contact among water, corncob and catalyst). A corncob dosage of 0.5 g was therefore selected as the optimal value.

From the above analysis, the optimal reaction conditions for xylose production were identified as 0.5 g MMCSA, 0.5 g corncob, and 50 mL deionized water under 150 °C for 2 h. Meanwhile, a parallel experiment was carried out and the error of xylose yield was about 2.4%. Fig. 5 also shows that arabinose could be generated under milder reaction conditions (*e.g.*, at lower temperature) than those used for xylose. Since arabinose is not the main product of hemicellulose degradation, its reaction behavior is not further discussed here.

The catalytic activity of MMCSA under the optimized reaction conditions is compared with those of other catalysts (Table 2). Compared with the results over Amberlyst-15⁴¹ and HZSM-5,⁴¹ a higher xylose yield was obtained in this study. A shorter reaction time was required in this work, to obtain a xylose yield similar to that attained with Gp-SO₃H-H₂O₂⁴¹ or C-SO₃H.⁴² Compared with Fe₃O₄/C-SO₃H,²⁷ the xylose yield was much higher when catalyzed by MMCSA under milder reaction conditions. These results indicated that the MMCSA catalyst showed higher catalytic activity than other catalysts tested in the literature so far. Moreover, the catalysts listed in Table 2 can be divided into three types: the first is the catalyst containing the -OH, -COOH and -SO₃H functional groups (*e.g.*, Gp-SO₃H-H₂O₂, Fe₃O₄/C-SO₃H, C-SO₃H and MMCSA); the second is that containing only one functional group of -SO₃H (*e.g.*, Amberlyst-15); and the last without any of the three functional groups (*e.g.*, HZSM-5). The xylose yield over different catalysts under their optimal reaction conditions indicated that -OH, -COOH and -SO₃H have combined catalytic effects on the hemicellulose degradation that could ensure a high xylose yield under mild reaction conditions.³⁹

3.6 Enzymatic hydrolysis of the pretreated residue

The changes in the components of the corncob are shown in Table 3. After pretreatment, the proportion of glucan in the

Table 4 Total sugar yields in the solid acid pretreatment and enzymatic hydrolysis processes

Process	Yield of saccharides (%)		
	Xylose	Glucose	Total sugar
Solid acid pretreatment ^a	74.9	7.6	90.4
Enzymatic hydrolysis ^b	83.5	95.2	

^a 150 °C, 2 h, 0.5 g of corncob, 0.5 g of the optimized MMCSA catalyst, and 50 mL of deionized water. ^b 40 FPU g⁻¹, 50 °C, 96 h.

Table 5 Comparison of enzymatic digestibility after solid acid pretreatment and other pretreatment methods

Raw material	Pretreatment method	Enzymatic hydrolysis	
		Time (h)	Digestibility (%)
Corncob	^a MMCSA ^{This work}	48	90.1
Corncob	^b LHW ³⁴	48	82.4
Sugarcane bagasse	^c HCl ⁴³	72	76.6
Sugarcane bagasse	^d LHW ⁴⁴	48	88.0
Sugarcane bagasse	^e NH ₃ ⁴⁵	48	95.0
Sugarcane bagasse	^f NaOH + LHW ³⁸	72	95.0
Sugarcane bagasse	^g NaOH ⁴⁵	72	85.0

Optimal pretreatment conditions: ^a 140 °C, 6 h, 0.25 g catalyst, 0.25 g corncob, 25 mL water. ^b 180 °C, 0.5 h, 12.5% (w/v) solid loading. ^c 130 °C, 10 min, 1.25% HCl, 12.5% solid loading. ^d 180 °C, 20 min, 5% solid loading, 4 MPa. ^e 160 °C, 20 min, 10% solid loading, 2 MPa. ^f 80 °C, 3 h, 20 mL 0.25 M NaOH, 180 °C, 20 min, 5% (w/v) solid loading. ^g 80 °C, 3 h, 20 mL 0.25 M NaOH, 1 g sugarcane bagasse. All results were calculated based on an enzyme loading of 40 FPU g⁻¹.

Fig. 7 SEM of corncob before (a) and after (b) pretreatment. Pretreatment conditions: 150 °C, 2 h, 0.5 g corncob, 0.5 g of the optimized MMCSA catalyst and 50 mL deionized water.

corn cob residue increased from 35.9% to 63.6% while the proportion of xylan dropped to only 8.6%. The hemicellulose removal rate reached 87.0%, but the removal rate of cellulose was only 8.3%, since most of the glucan was preserved while most of the xylan and some of the lignin were removed.

From Fig. 6, it is obvious that the enzymatic digestibility of the pretreated corn cob was higher than that of the raw material. Under an enzyme dosage of 20 FPU g^{-1} , the enzymatic digestibility of the raw material was 47.6% at 48 h and 53.1% at 96 h, whereas the enzymatic digestibility of the pretreated corn cob was increased to 80.4% at 48 h and 88.6% at 96 h. At a higher enzyme dosage of 40 FPU g^{-1} , the enzymatic digestibility of the pretreated corn cob increased more significantly to 90.1% after only 48 h, while the enzymatic digestibility of the raw corn cob was only 56.3% under the same conditions. Compared with the enzymatic hydrolysis result of the untreated corn cob at 48 h, the increasing rate of enzymatic digestibility was 68.9% at 20 FPU g^{-1} and 60.0% at 40 FPU g^{-1} for the pretreated corn cob at 48 h, indicating that the carbon-based solid acid pretreatment process could effectively improve the enzymatic digestibility. The yields of xylose and glucose from the optimal pretreatment (eqn (1)) and enzymatic hydrolysis (eqn (2)) of corn cob and the total sugar yield (eqn (3)) are shown in Table 4. The total sugar yield reached 90.4%.

The enzymatic digestibility of the residues after the solid acid pretreatment is compared with those from the other pretreatment methods (*i.e.*, liquid hot water, dilute acid and alkali treatment), as listed in Table 5. The enzymatic digestibility of corn cob was only 82.4% after liquid hot water pretreatment at 180°C .³⁴ Enzymatic hydrolysis of the sugarcane bagasse residue subject to 1.25% HCl pretreatment did not provide a very satisfactory result either: it yielded only 76.6% enzymatic digestibility from the decomposition of cellulose during the pretreatment process.⁴³ The enzymatic digestibility of sugarcane bagasse reached 88.0% after pressurized liquid hot water pretreatment,⁴⁴ and 95.0% after pressurized pretreatment by 25% NH_3 , 1.0% NaOH, and liquid hot water pretreatment.⁴⁵ When only NaOH was used for the pretreatment of sugarcane bagasse, the enzymatic digestibility reached 85% at 72 h. However, these pretreatment methods were complicated and might cause environmental pollution. In contrast, the current pretreatment method could provide the enzymatic digestibility of 90.1%, which is close to the highest value reported. Meanwhile, the efficiency of enzymatic digestibility was better than the other methods, and the pretreatment process using the carbon-based solid acid does not cause device corrosion, nor does it generate a large amount of waste water which is difficult to treat.

In order to explain the high enzymatic hydrolysis rate found in this work, the morphologies of corn cob and its residue after solid acid pretreatment were analyzed. As shown in Fig. 7, the surface of the raw corn cob was relatively smooth and dense, whereas the structure of its counterpart was deconstructed after the hydrolysis reaction in the pretreatment. The surface of the pretreated corn cob became loose and rough, containing several pores with relative sizes in the micrometer range. The changes

in the morphology of the corn cob indicate that the solid acid pretreatment process destroyed its surface topography and effectively improved the accessibility of cellulose and cellulase.

In order to more directly illustrate the causes of the enhanced enzymatic digestibility of the corn cob pretreated by

Fig. 8 Comparison of the structural differences between the raw and pretreated corncobs. (a) Maps of the cell wall thickness of the raw and pretreated corncobs; (b) 3D reconstruction of the raw (left) and pretreated (right) corncobs; (c) histogram of pore surface areas from the raw (untreated) and pretreated corncob particles.

MMCSA, 3D X-ray microscopy was used to characterize the structural changes of the corncob during these two hydrolysis steps (*i.e.*, in the solid acid pretreatment step and the subsequent enzymatic digestion step). As presented in Fig. 8(a), the thicknesses of the cell walls were computed for the raw and pretreated corncobs. The average thicknesses of the raw and pretreated corncobs were 8.1 μm and 3.9 μm , respectively (see the enhanced bright area in Fig. 8(a)). After pretreatment, the structure of the cell wall became continuous and homogeneous with the decrease of cell wall thickness, which is consistent with the previous finding (Table 3) that most hemicellulose and some lignin were removed during the pretreatment process.⁴⁶

The number of pores within the particles and their surface area can be calculated by 3D X-ray microscopy. As shown in Fig. 8(b), the porosities of the raw and pretreated corncobs were 63.4% and 48.7%, respectively. Fig. 8(c) shows the surface area distribution of pores of the raw and pretreated corncobs. The pore surface area is defined on a logarithmic scale in terms of square microns. In the raw corncob, most part of the pore surface area was distributed in the range of 3–10 μm^2 ; these accounted for almost 63.4% of the total pores in the corncob. In the pretreated corncob, however, the largest peak appeared in the pores with surface areas greater than 200 μm^2 , these accounted for almost 48.7% of the total pores. The main reason for the decrease in the porosity after pretreatment is that the corncob structure collapsed with the dissolution of the components of the corncob during the pretreatment process, which resulted in the original pores becoming macropores after being connected in series. Thus, the physically accessible surface area became larger after pretreatment, a condition beneficial to improving the rate of enzymatic hydrolysis.⁴⁷

More specifically, a series of irregular holes and folds occurred on the corncob after the pretreatment, which represents a situation beneficial for the enhancement of cellulose accessibility by the dissolution of hemicellulose and the removal of lignin.⁴⁸

4. Conclusion

A new magnetic carbon-based solid was synthesized *via* a simple and inexpensive impregnation–carbonization–sulfonation method. This catalyst showed high xylose selectivity during corncob hydrolysis, with a xylose yield of 73.4% and a cellulose retention of 91.7% under the optimized reaction conditions (150 °C, 2 h, 0.5 g of corncob, 0.5 g of the optimized MMCSA catalyst and 50 mL of deionized water.). The corncob residue was easily separated out of the solid catalyst by applying an external magnetic field. Enzymatic digestibilities of the residue at 90.1% and 95.2% were achieved at 48 h and 96 h (5% substrate concentration (w/v), 50 °C, with cellulose loading at 40 FPU g^{-1}), respectively. Based on this two-step hydrolysis, a total sugar yield of 90.4% was achieved. The combination of carbon-based solid acid hydrolysis of hemicellulose and enzymatic hydrolysis of cellulose could thus fully depolymerize corncob, which shows a potentially efficient and sustainable utilization of lignocellulose.

Conflicts of interest

There are no conflicts to declare.

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