

## A Two-Step Conversion of Corn Stover into Furfural and Levulinic Acid in a Water/Gamma-Valerolactone System

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A two-step hydrolysis method was evaluated as a potential means of obtaining high yields of furfural and levulinic acid from corn stover using sulfuric acid as catalyst in a water/gamma-valerolactone (GVL) system. The corn stover underwent a high-temperature hydrolysis process to produce levulinic acid, followed by a low-temperature hydrolysis process to produce furfural. A series of experiments were conducted to explore the relationship between the different reaction parameters and the final yields of furfural and levulinic acid. Scanning electron microscopy (SEM) pictures together with X-ray diffraction (XRD) analysis were used to further elaborate on the hydrolysis results. Molar yields of about 70.65% furfural and 57.7% levulinic acid were obtained by applying this method with a low temperature of 140 °C and a high temperature of 190 °C, together with 0.2 M of sulfuric acid used as the catalyst. These results indicated that this was an effective way to obtain satisfactory yields of furfural and levulinic acid from corn stover.

*Keywords:* Two-step conversion; Corn stover; Furfural; Levulinic acid;  $\gamma$ -Valerolactone

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### INTRODUCTION

In recent years, increasing awareness of the need to decrease the environmental footprint of society has resulted in great enthusiasm for utilizing biomass, which is a sustainable alternative source of carbon that could feasibly meet the increasing demands for biofuels and bio-chemicals in the future (Huang *et al.* 2011; Dutta and Pal 2014; Ioelovich 2015). To that end, extensive research has been focused on the effective conversion of lignocellulosic biomass into fuels and chemicals (Cherubini 2010; Zu *et al.* 2014; Zhang *et al.* 2015; Maity 2015). With the rapidly expanding field of lignocellulosic biomass conversion, several platform chemicals have been identified as promising building blocks for the bio-refinery industry; among these candidates, furfural and levulinic acid (LA) have received increasing interest (Cai *et al.* 2014; Qi *et al.* 2014). Furfural, which is derived from pentose, has been widely used as a solvent in the petroleum industry and is a precursor for many furan-based chemicals, such as furfuryl alcohol, furoic acid, maleic anhydride tetrahydrofuran, and phenolics (Lange *et al.* 2012). Furfural also holds great potential for the production of “drop in” fuels such as dimethylfuran or ethyl levulinate, which can be produced by polymerization (Yan *et al.* 2014; Bohre *et al.* 2015). Levulinic acid, which is derived from hexose through the intermediate 5-hydroxymethylfurfural

(HMF), has been identified by the U. S. Department of Energy as one of the top 12 high-potential and versatile platform chemicals (Werpy and Petersen 2004). Levulinic acid has been commonly used as an additive in medicine, food, agriculture, and cosmetics (Van de Vyver *et al.* 2011; Galletti *et al.* 2012; Yan *et al.* 2015). Furthermore,  $\gamma$ -valerolactone (GVL), a hydrogenation derivative of levulinic acid, is also an important biomass-derived platform chemical (Wright and Palkovits 2012; Alonso *et al.* 2013a; Ding *et al.* 2014). GVL is frequently used as an additive for food and drug applications, gasoline, or as a solvent, and it is also the precursor for a series of high-value chemicals, such as isomers of butenes, methyl-tetrahydrofuran, 2-MeTHF, *etc.* (Mehdi *et al.* 2008). As two of the most promising building block chemicals, furfural from hemicellulose and levulinic acid from cellulose have received considerable attention as sustainable sources of valuable intermediates.

Comprehensive studies have been carried out on the production of furfural and levulinic acid from lignocellulosic biomass, which is typically made up of hemicellulose, cellulose, and lignin. Hemicellulose, an amorphous heteropolymer, contains both linear and branched pentose and can be hydrolyzed into primarily xylan and xylose, as well as minimal amounts of arabinose, galactose, *etc.*, after which the xylose can be converted to furfural by dehydration. Cellulose, with a highly organized crystalline fibrous structure consisting of linear homopolymers of glucose, can be hydrolyzed into polysaccharides and monosaccharides and then converted into equimolar amounts of LA and formic acid (FA) through the intermediate HMF (Van Dam *et al.* 1986). Both of these reaction processes need acid as a catalyst, and numerous kinds of mineral acids, organic acids, solid acids, and heteropoly acids have been investigated in light of the need to obtain high yields of furfural and LA (Kootstra *et al.* 2009; Gallo *et al.* 2013). Ionic liquids as solvents (Aishah and Amin 2013) and chlorinated salts as additives (Shen *et al.* 2014; Zhang *et al.* 2014) have been used to enhance the hydrolysis product yields. Furthermore, a biphasic system containing an aqueous phase and an organic phase for the hydrolysis reaction has been proposed (Wettstein *et al.* 2012; Han *et al.* 2014). The aqueous phase, or modified aqueous phase, is used as the reaction phase for acid-catalyzed conversions of the substrate to the target product, while the organic phase extracts the target product from the organic phase and prevents its degradation. Various organic solvents have been applied as the organic phase, such as THF, DMSO, MIBK, GVL, *etc.* Moreover, it is widely accepted that GVL has been proclaimed a “green solvent” for comprehensive applications (Horváth *et al.* 2008). GVL, as an organic phase in a biphasic system, exhibits considerable advantages in accelerating the cellulose conversion rate and minimizing the degradation of furfural, solubilizing the humins formed during the process and simplifying the separation steps (Alonso *et al.* 2013b; Mellmer *et al.* 2014). Nonetheless, when it comes to real lignocellulosic biomass in one-pot hydrolysis reactions, the optimal hydrolysis conditions for furfural and levulinic acid are different. More specifically, furfural generation requires a moderate acid concentration and reaction temperature, whereas levulinic acid generation requires much tougher reaction conditions in which furfural is readily degraded (Alonso *et al.* 2013b). Thus, the optimal reaction conditions for furfural may lead to a minimal yield of levulinic acid, while suitable reaction conditions for levulinic acid will give rise to furfural degradation. The challenges posed by the different hydrolysis reaction conditions that are optimal for hemicellulose and cellulose make it cumbersome and difficult to obtain high yields of both furfural and levulinic acid in a one-pot reaction, even with the use of GVL.

In this study, a two-step method is proposed to improve the aforementioned dilemma by rendering cellulose and hemicellulose hydrolyzed under their respective optimal conditions, thus allowing a high yield of levulinic acid and furfural to be obtained in the same hydrolysate liquid. A set of hydrolysis devices consisting of a high temperature reactor and a low temperature reactor was used in the hydrolysis process. The substrate underwent a high-temperature hydrolysis to generate a high yield of levulinic acid, followed by a low temperature hydrolysis, using the hydrolysate liquid from the former step, to generate a high yield of furfural. Thus, after the two-step hydrolysis the hydrolysate liquid contained a high yield of both furfural and levulinic acid. Compared with published relevant studies applying one-pot reactions (Alonso *et al.* 2013b; Cai *et al.* 2013), which resulted in either a high yield of furfural or a high yield of levulinic acid, a more balanced high yield of furfural and levulinic acid was obtained by this two-step method. In addition, according to previous reports, the hydrolysis efficiency of sulfuric acid and hydrochloric acid used as a catalyst may vary with the raw material (Herrera *et al.* 2004; Meinita *et al.* 2012). Thus, different mineral acids, as well as different temperatures and acid concentrations, were also investigated to optimize the hydrolysis reaction. Finally, scanning electron microscopy (SEM) and X-ray diffraction (XRD) analyses were applied to verify the hydrolysis results.

## EXPERIMENTAL

### Materials

The corn stover was harvested in the Northern Anhui Province of China and was ground using a high-speed rotary cutting mill, passed through a 40-mesh screen, washed with tap water to get rid of the dust, and oven-dried at 333 K to a constant weight. The corn stover powder was stored in a tightly closed plastic bottle at ambient temperature.

The 5-hydroxymethylfurfural (HMF, 99%), furfural (98%), and  $\gamma$ -valerolactone (98%) used as standard samples were purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). The HCl, H<sub>2</sub>SO<sub>4</sub>, and H<sub>3</sub>PO<sub>4</sub> were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The Aminex HPX-87H column was purchased from Bio-Rad Laboratories Inc. (Hercules, CA, USA). The Waters Symmetry®-C18 column was purchased from Waters Corporation (Milford, MA, USA).

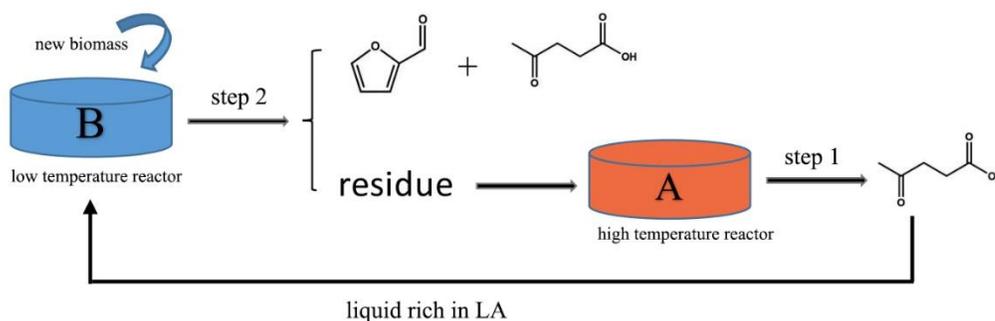
### One-Step Process for Corn Stover Hydrolysis

Milled corn stover (dry basis) was mixed with water/GVL (1:4) in a solid to liquid ratio of 1:15. The slurry was electrically heated to the target temperature in a stainless steel reactor with mechanical agitation. After the reaction, the reactor was immediately quenched in tap water. Different acids (hydrochloric acid, sulfuric acid, and phosphoric acid) with equimolar H<sup>+</sup> concentrations and different reaction temperatures (from 130 °C to 180 °C) were investigated. After the reaction was completed, the hydrolysate was collected, the residue was washed away with distilled water, and finally the liquid mixture was analyzed using a high-performance liquid chromatography (HPLC) system (Waters 515 pump, Waters 2489 UV/Visible Detector, Waters 2414 refractive index detector) to determine the yields of the products.

### Two-Step Conversion Process for Corn Stover

A set of hydrolysis reactors, constituting two individual stainless steel reactors

(high-temperature reactor A and low-temperature reactor B), was used in this process (Fig. 1). In a typical experiment, the solids collected from the low temperature reaction, a certain amount of sulfuric acid, 10 mL of water, and 40 mL of GVL was mixed in reactor A, where it underwent high-temperature hydrolysis to obtain a high yield of levulinic acid. After the reaction, the liquid and solid components were separated, and the liquid component, which was rich in levulinic acid, together with 3.3 g of new biomass, was transferred to reactor B, where it underwent low-temperature hydrolysis. After the two-step hydrolysis, the liquid component contained a high yield of both furfural and levulinic acid, which was collected, and the target products were separated by distillation. The residue, which was rich in cellulose, was transferred to reactor A for another high-temperature reaction. After the reaction, the water-GVL mixture was normally monophasic; however, it could be separated into an organic phase and a water phase after adding some supercritical carbon dioxide to it. As the furfural and levulinic acid were mainly present in the organic phase, thus furfural, GVL, and levulinic acid can be separated through reduced pressure distillation. The furfural and levulinic acid were collected as final product, and GVL can be recycled as solvent in a new reaction. The initial solid component used as the substrate for Step 1 was prepared prior to the whole reaction flow under the same low reaction temperature as Step 2, and the furfural and levulinic acid generated here were excluded from the final yields. Once the optimal reaction conditions were determined, such an initial step acts as the restart point of a recycled reaction flow.



**Fig. 1.** The reaction process of the two-step hydrolysis method

To further elaborate on the effects of different temperatures and acid concentrations on the final product yields, low temperature conditions ranging from 120 °C to 140 °C, high temperature conditions ranging from 160 °C to 200 °C, and sulfuric acid concentrations ranging from 0.1 M to 0.3 M were tested.

## Analysis Methods

### *Quantification procedure for furfural, HMF, and levulinic acid*

The quantities of furfural and HMF were determined using HPLC (described above) with a Waters Symmetry®-C18 column (5 μm, 4.6 × 150 mm) and an Ultraviolet Detector (Waters 2489) at 280 nm. The temperature of the column oven was maintained at 30 °C, and water/methanol (3:2, V/V) with a flow rate of 0.4 mL/min was chosen as the mobile

phase. The quantity of levulinic acid was determined using an Aminex HPX-87H column (9  $\mu\text{m}$ , 7.8  $\times$  300 mm) and a Refractive Index Detector (Waters 2414), with the column oven and detector temperature set at 63  $^{\circ}\text{C}$  and 50  $^{\circ}\text{C}$  respectively, and 0.005 M  $\text{H}_2\text{SO}_4$  at a flow rate of 0.6 mL/min used as the mobile phase. The HMF, furfural, and levulinic acid detected in both steps were counted together as the final yields.

The yields of HMF, furfural, and levulinic acid were defined as follows:

$$\text{HMF (\%)} = (\text{moles of HMF})/(\text{moles of glucose in corn stover}) \times 100 \quad (1)$$

$$\text{Furfural (\%)} = (\text{moles of furfural})/(\text{moles of xylose in corn stover}) \times 100 \quad (2)$$

$$\text{LA (\%)} = (\text{moles of LA})/(\text{moles of glucose in corn stover}) \times 100 \quad (3)$$

### Scanning electron microscopy (SEM)

SEM pictures were taken at 2000X magnification to identify changes to the surface structure of untreated, low-temperature treated, and high-temperature treated corn stover. A JEOL JSM-6510 scanning electron microscope (Tokyo, Japan) was used. The wet hydrolysate solid residues were dried in a vacuum freeze drier for 36 h to preserve their surface texture, and prior to the examination, all the samples were sputter-coated with a thin layer of gold.

### X-ray analysis of the solid residues

To further probe into the mechanism of internal transformations, X-ray diffraction (XRD) was performed to investigate the physical characteristics of the untreated and treated corn stover. X-ray diffraction analysis elucidates changes in terms of the crystallinity index, which is a key measurement that compares the crystalline region to the amorphous region, allowing possible explanations for the hydrolysis results. The XRD analysis was carried out using a Rigaku TTR-III X-ray instrument (Tokyo, Japan), and the samples were scanned at a speed of 8 $^{\circ}$ /min, in the range of  $2\theta = 5^{\circ}$  to  $40^{\circ}$ , with a step size of 0.02 $^{\circ}$  and at room temperature.

The crystallinity index was defined as previously described (Hall *et al.* 2010),

$$CrI = \frac{I_{002} - I_{am}}{I_{002}} \times 100\% \quad (4)$$

Where  $I_{002}$  and  $I_{am}$  are the intensities of diffraction at  $2\theta = 22.6^{\circ}$  (crystalline region) and  $2\theta = 18.4^{\circ}$  (amorphous region), respectively.

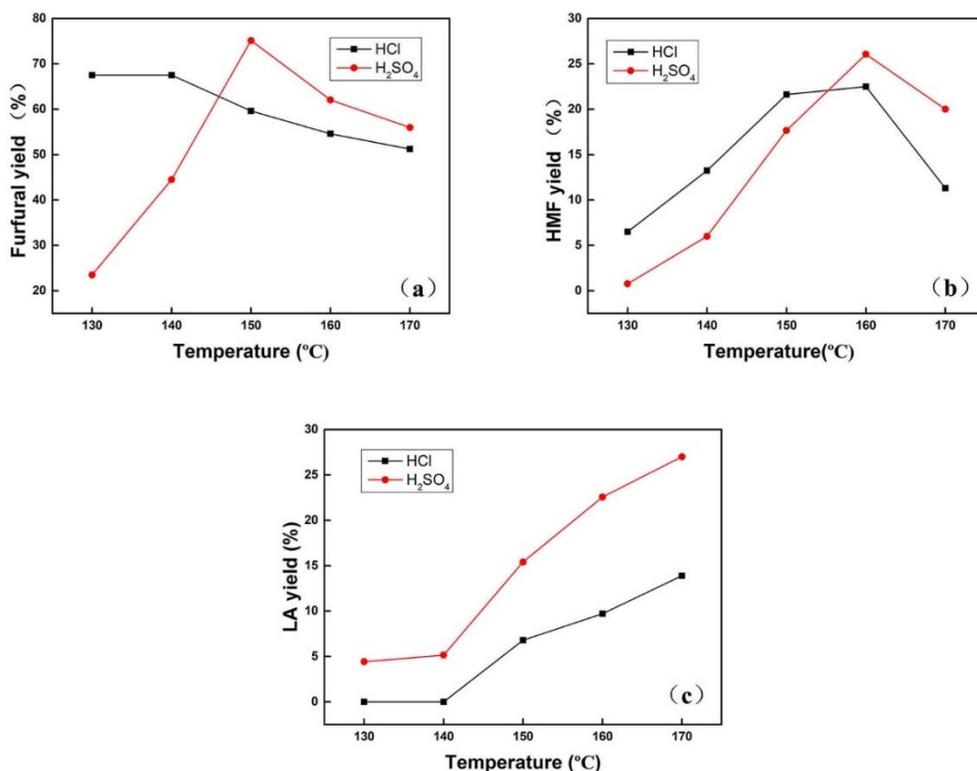
## RESULTS AND DISCUSSION

The corn stover used in the experiment was identical to that used in previous research (Zu *et al.* 2013), and the chemical composition was determined as follows: 39.6% glucan, 19.5% xylan, 2.0% arabinan, 1.2% galactan, 19.1% acid-insoluble lignin, 3.1% ash, and 15.5% other components. The furfural yield was calculated based on the C5 fraction, and the levulinic acid yield was calculated based on the C6 fraction.

### Hydrolysis Performance of Different Mineral Acids Used as Catalysts

$\text{H}^+$  plays a significant role in the hydrolytic conversion of hemicellulose to furfural

and cellulose to levulinic acid, and previous reports have also suggested that the presence of chloride ions favors xylose dehydration into furfural and glucose isomerization into fructose, facilitating the downstream conversion to HMF. Hydrochloric acid is the preferred acid for this application among other strong Brønsted acids (Marcotullio and De Jong 2010; Dallas Swift *et al.* 2015). However, for the conversion of both hemicellulose and cellulose, the effect of different mineral acids on the final yield has not been widely reported, and there are some contradictions between recent reports (Herrera *et al.* 2004; Meinita *et al.* 2012). Thus, different mineral acids were investigated to determine the optimal acid to use as a catalyst. Figure 2 shows the results for the hydrolysis of corn stover under the same hydrogen ion concentration (0.2 mol/L) using hydrochloric acid and sulfuric acid. In agreement with previous research, using HCl as a catalyst resulted in a considerably higher yield of furfural at the relatively low temperature of 130 °C. Because the furfural is readily degraded under high temperatures, the yield of furfural decreased progressively with the increase in temperature. In contrast, the HMF yield showed a different tendency when compared with furfural, increasing sharply from 130 °C to 150 °C and decreasing gradually as a consequence of LA formation. Below 140 °C, LA could scarcely be detected, but later increased with the rise of temperature, indicating that high temperature was of great importance to LA formation.



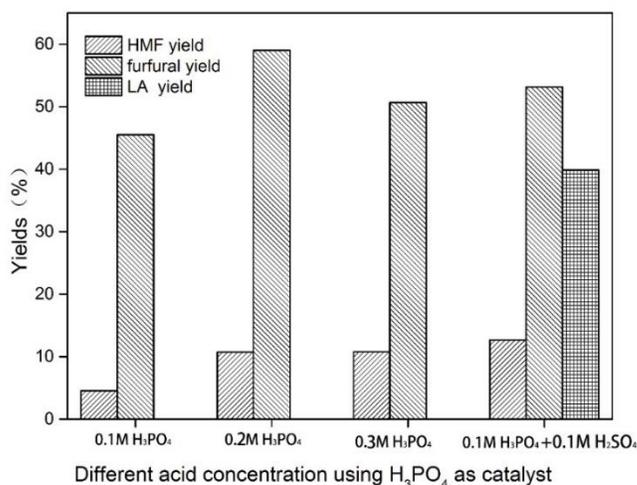
**Fig. 2.** The hydrolysis performance of 0.2 M of HCl and 0.1 M of H<sub>2</sub>SO<sub>4</sub> under different temperatures with a reaction time of 90 min. (a) furfural yield; (b) HMF yield; (c) LA yield

The sulfuric acid catalyst demonstrated that similar rules governed the HMF and LA yields; however, the LA yield was dramatically higher (almost twofold) than that obtained with hydrochloric acid at the same temperature, which indicated that sulfate ions may have played an important role in the conversion of cellulose to LA. The furfural yield

increased with temperature and reached a peak (75.12%) at 150 °C, but higher temperatures decreased the yield of furfural.

In contrast, a high furfural yield was obtained at 130 °C (67.51%) with hydrochloric acid, which suggested that hydrochloric acid was more efficient in producing furfural. However, to compensate for the extra energy cost due to the difference in reaction temperatures, sulfuric acid might be a better catalyst for this reaction due to its higher furfural yield.

In addition to hydrochloric acid and sulfuric acid, phosphoric acid at different concentrations (0.1 M, 0.2 M, and 0.3 M) under the temperature of 170 °C was also tested (Fig. 3). Using phosphoric acid alone as catalyst yielded no levulinic acid; however, when 0.1 M of phosphoric acid was combined with 0.1 M of sulfuric acid, an LA yield of approximately 40% was obtained, which was higher than the yield measured using 0.1 M sulfuric acid (27%) but lower than that using 0.2 M sulfuric acid (57.26%) (Fig. 4). This result indicated that sulfate ions enhance the final product of levulinic acid.



**Fig. 3.** Effects of phosphoric acid concentration on furfural, HMF, and LA yield under 170 °C with a residence time of 90 min

**Table 1.** Effect of Sulfuric Acid and Hydrochloric Catalysts on Glucose Substrate

Acid Dosage	Glucose Conversion (%)	HMF Yield (%)	LA Yield (%)
0.1 M HCl	95.30	16.25	26.00
0.2 M HCl	96.11	9.06	26.78
0.3 M HCl	96.64	2.88	30.29
0.05 M H <sub>2</sub> SO <sub>4</sub>	95.99	6.68	41.45
0.15 M H <sub>2</sub> SO <sub>4</sub>	96.78	3.04	51.73
0.2 M H <sub>2</sub> SO <sub>4</sub>	96.02	1.16	53.74
Reaction conditions: 1.44 g glucose, 170 °C, 90 min			

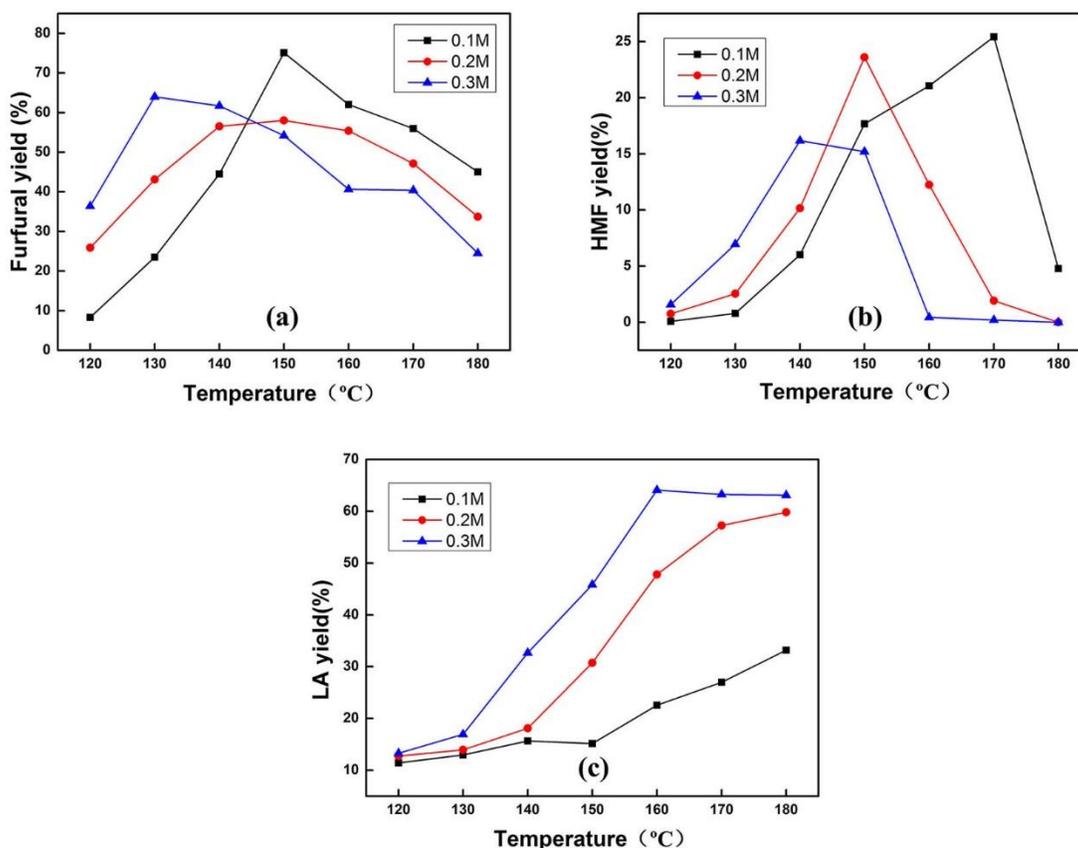
To further probe into the possible mechanism of how different anions affect the final yield of levulinic acid, equal moles of glucose and HMF were used as substrates under reaction conditions of 170 °C and 90 min (Tables 1 and 2). The results suggested that the sulfuric acid catalyst is superior to hydrochloric acid due to its higher selectivity in terms of HMF conversion to levulinic acid.

**Table 2.** Effect of Sulfuric Acid and Hydrochloric Acid Catalysts on HMF Substrate

Acid Dosage	HMF Conversion (%)	LA Yield (%)	LA Selectivity (%)
0.1 M HCl	70.26	31.13	44.31
0.2 M HCl	81.45	33.13	40.68
0.3 M HCl	90.45	36.94	40.84
0.05 M H <sub>2</sub> SO <sub>4</sub>	86.30	77.76	90.10
0.15 M H <sub>2</sub> SO <sub>4</sub>	86.76	79.50	91.70
0.2 M H <sub>2</sub> SO <sub>4</sub>	93.73	88.71	94.64

Reaction conditions: 1.0 g HMF, 170 °C, 90 min

In light of these results, it was postulated that both H<sup>+</sup> and anion species induced a change in the corn stover hydrolysis, and SO<sub>4</sub><sup>2-</sup> seemed to have been mainly responsible for LA generation. Thus, sulfuric acid was chosen as the catalyst for this experiment.



**Fig. 4.** Effect of different acid concentrations and temperatures on final yield in a one-step reaction system. (a) furfural yield; (b) HMF yield; (c) LA yield

### Effects of Sulfuric Acid Concentration and Temperature on Final Yields with One-Step Hydrolysis

The effects of sulfuric acid concentration (0.1 M, 0.2 M, and 0.3 M) and reaction temperature (from 120 °C to 180 °C) on furfural, HMF and LA production were investigated in a reaction lasting 90 min (Fig. 4). The optimum temperature for furfural production varied with acid concentration; specifically, 0.1 M of sulfuric acid and 150 °C

resulted in a maximum furfural yield within the scope of the experiment of 75.12%. With 0.3 M of acid, the corresponding temperature for furfural was 130 °C, and the maximum yield declined to 64%. This result indicated that the acidic environment was crucial for hemicellulose hydrolysis, but excessive H<sup>+</sup> accelerated furfural degradation (Fig. 4a). As an intermediate for the conversion of glucose to levulinic acid, HMF yield increased remarkably with the increase of reaction temperature in the range of 120 °C to 150 °C, which might reflect that cellulose hydrolysis requires tougher conditions than hemicellulose.

When the reaction temperature was around 150 °C, most hemicellulose was converted into furfural, while this temperature was not sufficient for cellulose conversion into levulinic acid. Moreover, as the temperature was increased, HMF was converted into levulinic acid, and thus the HMF yield increased first and decreased later with increasing reaction temperature (Fig. 4b).

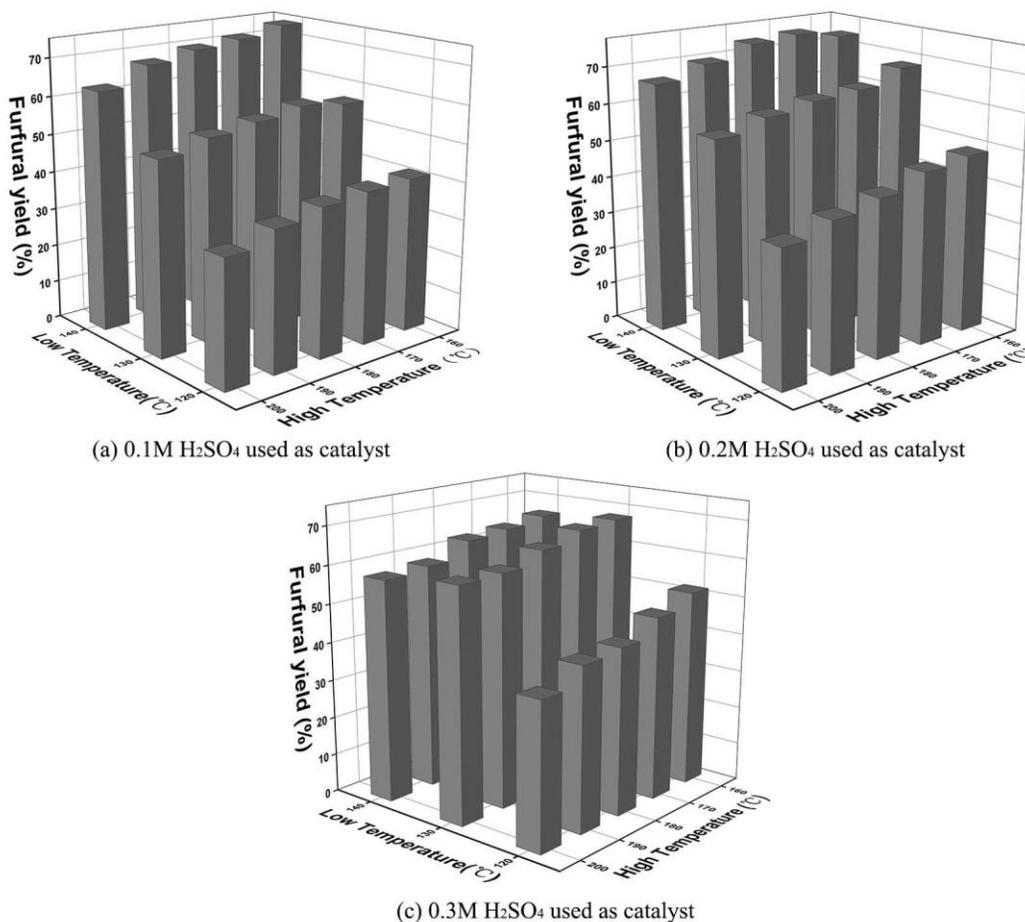
Higher temperatures and higher acid concentrations both contribute to increased levulinic acid yield, and the highest yield within the experimental scope was 64.08%. This was obtained at 160 °C with 0.3 M of sulfuric acid catalyst and remained steady with increasing temperature (Fig. 4c). It is apparent from Fig. 4 that the high yields of furfural and levulinic acid could not be obtained at the same time in a one-step hydrolysis. Namely, when the levulinic acid yield reached 64.08%, the corresponding furfural yield was only 40.64%, and when furfural yield reached 75.12%, the levulinic acid was merely 15.41%. The optimal hydrolysis conditions for furfural were not suitable for levulinic acid and *vice versa*.

Considering these results, it was concluded that furfural production requires low acid concentrations and medium temperatures, while levulinic acid generation requires relatively high acid concentrations and high temperature to occur. The non-overlapping optimal reaction conditions pose a challenge to obtaining high yields of both furfural and levulinic acid simultaneously in a one-step reaction system; therefore, a two-step conversion method was proposed.

### Hydrolysis Performance of Two-Step Conversion Method

In the two-step conversion method described in the experimental section, the reaction was carried out at a high temperature followed by a low temperature. Figures 5 to 7 demonstrate the relationship between furfural, HMF, and levulinic acid yields at the low temperature and high temperature adopted in the two-step conversion. In the one-step process, a reaction temperature above 150 °C was found to be the best condition for obtaining a relatively high yield of levulinic acid. Thus, the high temperature applied for the first step was set between 160 °C and 200 °C, and the low temperature applied for the second step was set between 120 °C and 140 °C.

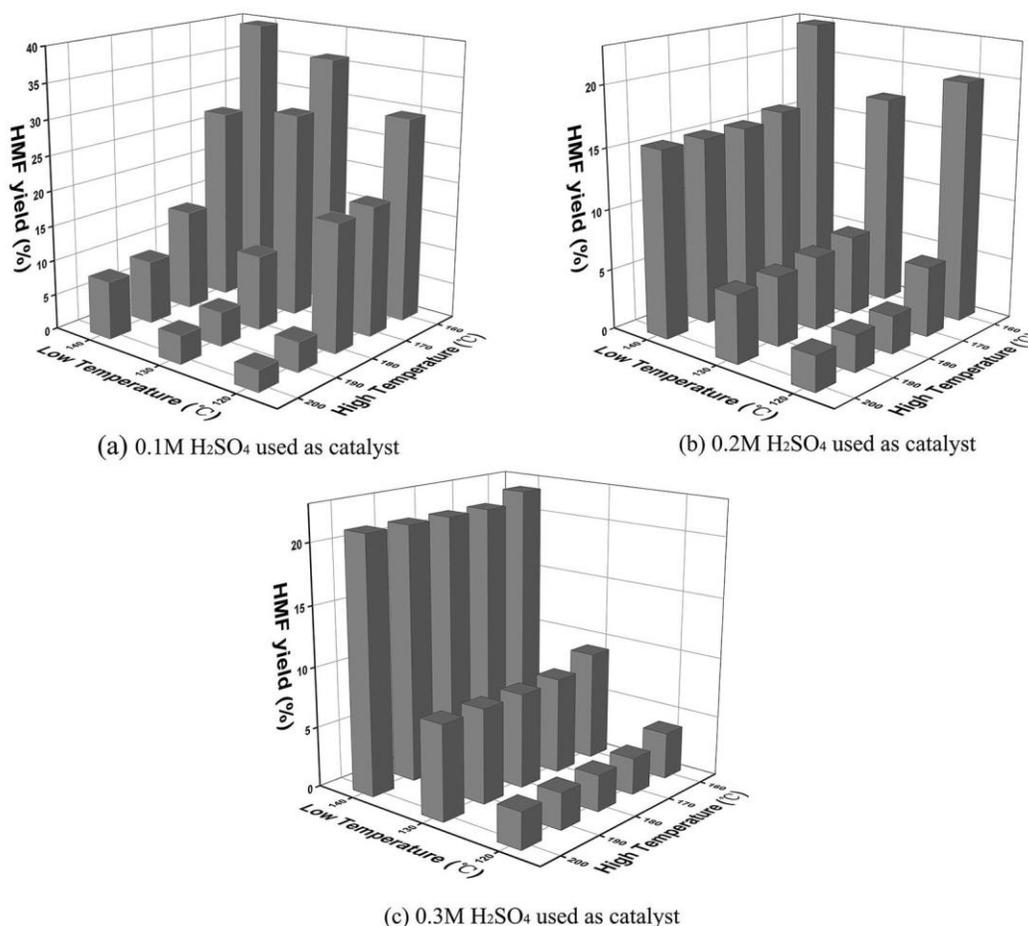
Figure 5 depicts the furfural yields under different acid concentrations and temperatures. Both of these variables strongly influenced the furfural yield. During the low temperature hydrolysis, increasing the temperature from 120 °C to 140 °C and the acid concentration from 0.1 M to 0.2 M effectively enhanced the furfural yield, while a further increase of acid concentration to 0.3 M caused furfural degradation. A high furfural yield (75.41%) was obtained when 140 °C and 0.2 M of sulfuric acid were used, which was quite similar to the best yield acquired from the one-step method.



**Fig. 5.** Effects of two-step hydrolysis conditions on furfural yield. The low temperature ranged from 120 °C to 140 °C, and the high temperature ranged from 160 °C to 200 °C. The sulfuric acid concentration ranged from 0.1 M to 0.3 M.

Figure 6 shows the HMF yields in the two-step conversion process. A high yield was usually obtained when the high temperature was set as 160 °C, which was also the beginning point for the downstream conversion to levulinic acid. It is notable that with the high acid concentration (0.3 M of sulfuric acid), almost all the HMF was produced in the low-temperature step, and scarcely any HMF was detected in the high-temperature step. At the same acid concentration of 0.3 M, the higher reaction temperature of 140 °C resulted in an HMF yield that was almost threefold that obtained at 130 °C, and six times higher than that obtained at 120 °C, indicating that acid concentration was what mainly contributed to the cellulose conversion to HMF, while temperature dominated the HMF conversion to levulinic acid.

Figure 7 shows that levulinic acid yield increased with acid dosage and reaction temperature. At low acid concentrations such as 0.1 M, the levulinic acid yield increased remarkably as the temperature rose from 160 °C to 200 °C. However, with higher acid concentrations such as 0.2 M and 0.3 M, a satisfactory levulinic acid yield could be achieved at 180 °C, and the increase in yield was minimal even when the temperature was increased, showing that 180 °C was the optimum reaction temperature for levulinic acid generation.

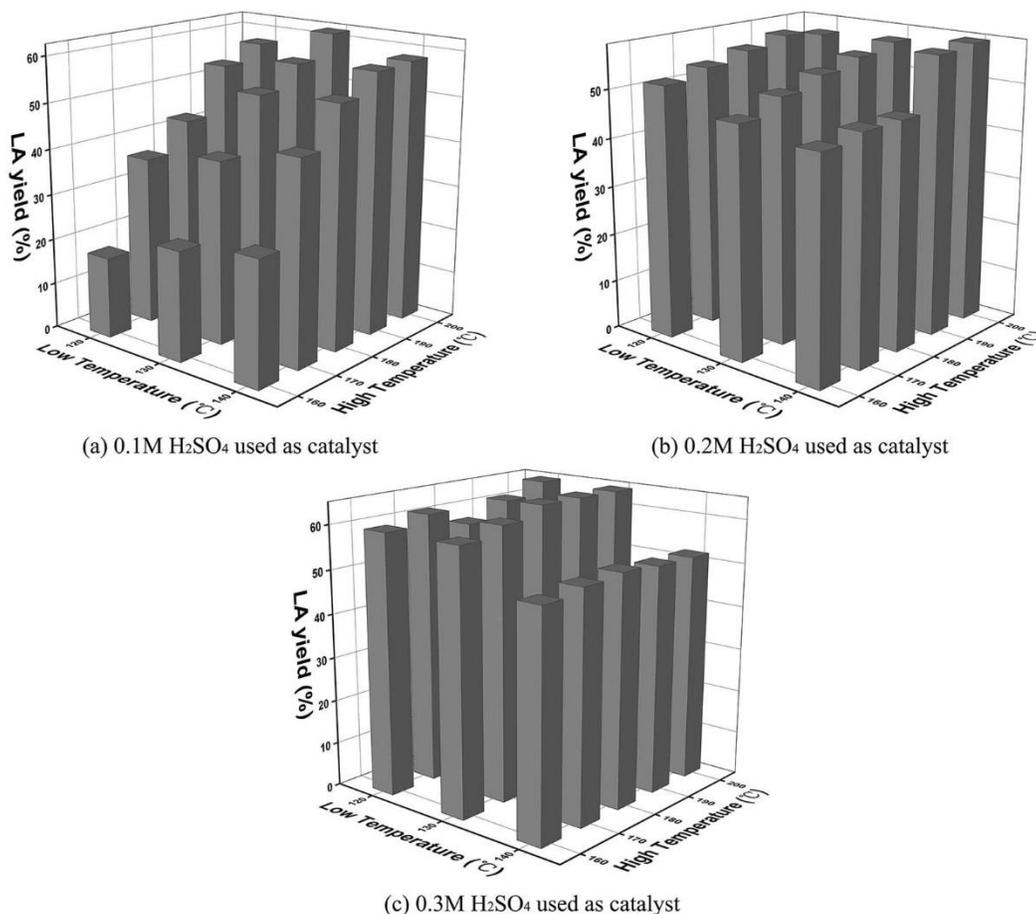


**Fig. 6.** Effects of two-step hydrolysis conditions on HMF yield. The low temperature ranged from 120 °C to 140 °C, and the high temperature ranged from 160 °C to 200 °C. The sulfuric acid concentration ranged from 0.1 M to 0.3 M.

With the two-step hydrolysis method, both hemicellulose and cellulose were hydrolyzed effectively under their respective optimal temperatures, and the water/GVL system partly dissolves the lignin, making the H<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> more accessible to hemicellulose and cellulose, providing an advantageous environment for corn stover depolymerization and dehydration. Thus, high yields of furfural (70.65%) and levulinic acid (57.7%) were achieved in this way. The threshold posed by the structural differences between hemicellulose and cellulose was reasonably overcome.

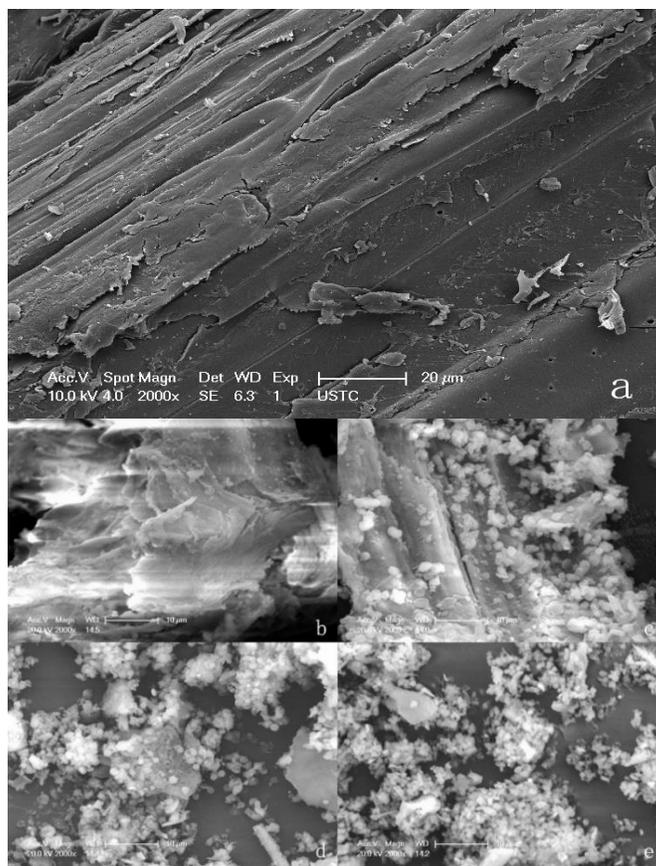
### Scanning Electron Microscopy (SEM) Analysis

SEM pictures of untreated corn stover and solid residues after low-temperature treatment (120 °C, 140 °C) and high-temperature treatment (160 °C, 200 °C) are shown in Fig. 8. The untreated corn stover exhibited a compact structure with tightly connected fibers composed of cross-linked hemicellulose, cellulose, and lignin. After low-temperature hydrolysis, the initial smooth surface was crumpled, and the microfibrils became somewhat fragmented after 120 °C treatment. As can be seen in Fig. 4, a molar yield of furfural of approximately 30% was obtained at 120 °C under 0.1 M of H<sub>2</sub>SO<sub>4</sub>, indicating that part of the hemicellulose was converted to furfural, which confirmed the SEM results.



**Fig. 7.** Effects of two-step hydrolysis conditions on LA yield. The low temperature ranged from 120 °C to 140 °C, the high temperature ranged from 160 °C to 200 °C, and the sulfuric acid concentration ranged from 0.1 M to 0.3 M.

Small, spherical particles of debris became visible when the temperature was raised from 120 °C to 140 °C, and the formation of these small, spherical debris particles increased the surface area of the substrate, leaving the cellulose more vulnerable to acid attack. Moderate yields of HMF and LA were obtained at this point, as shown in Fig. 6 and 7, indicating that part of the cellulose was hydrolyzed at 140 °C. With the increase of temperature to 160 °C and 200 °C, the amount of spherical debris particles increased dramatically, and the whole surface of the corn stover cracked into pieces. This result may have indicated a higher level of hydrolysis in which most hemicellulose and relatively amorphous cellulose were converted to furfural and levulinic acid, leaving the core crystalline region of the cellulose, which is very difficult to hydrolyze. The experimental data was aligned with such assumptions. Levulinic acid reached a plateau after a certain high-temperature step and remained steady even with the increase of temperature, but furfural yield decreased with the rising temperature due to degradation. For instance, Fig. 5 and 7 show that the LA yield remained almost constant from 160 °C to 200 °C under 0.3 M acid concentration and at the low temperature of 140 °C. In contrast, furfural yield gradually decreased with the rise of temperature. Further certification of this result was given by XRD analysis.



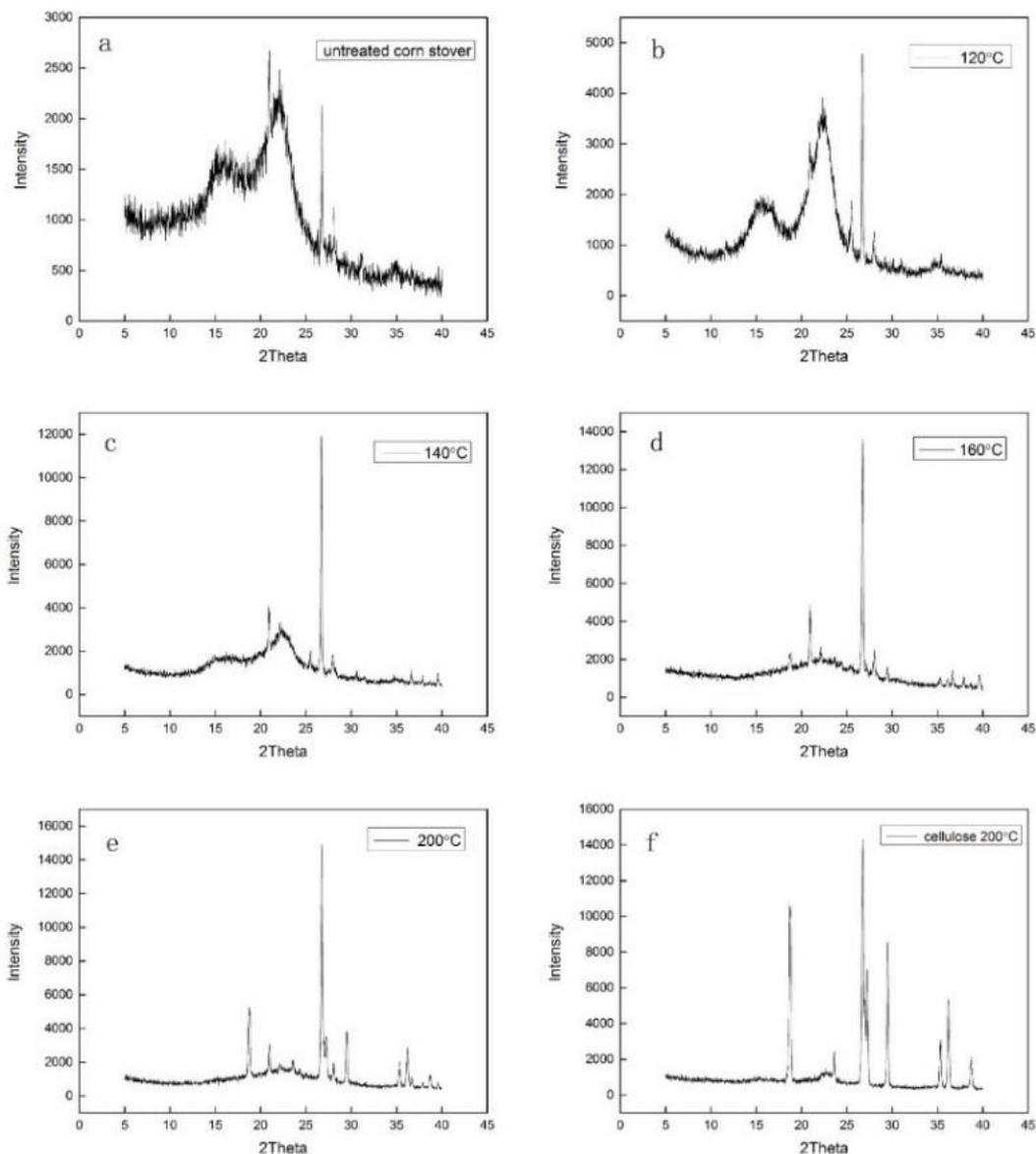
**Fig. 8.** SEM of treated and untreated corn stover at 2000x magnification. (a) untreated; (b) 120 °C treated; (c) 140 °C treated; (d) 160 °C treated; (e) 200 °C treated. The samples are from two-step hydrolysis under 0.2 M sulfuric acid treatment.

### X-ray Diffraction (XRD) Analysis

The crystallinity index, which is the relative measurement of diffraction intensity in the crystalline region compared with the amorphous region, can significantly affect biomass hydrolysis. The crystallinity index is influenced by the biomass composition, in which cellulose forms the backbone of lignocellulose and is embedded in a matrix of hemicellulose and lignin. Cellulose is regarded as mainly crystalline, while lignin and hemicellulose are considered amorphous. Thus, an increased crystallinity index could represent the removal of amorphous structures in biomass. In addition to a highly ordered crystalline region, cellulose also contains a para-crystalline region and a relatively amorphous region that can be readily hydrolyzed, while the highly crystalline region, usually buried deeply in the complex structure of lignocellulose, is very cumbersome to hydrolyze (Kanchanalai *et al.* 2016).

Figure 9 shows the XRD patterns of untreated samples and those treated at 120 °C, 140 °C, 160 °C, and 200 °C, as well as  $\alpha$ -cellulose samples treated at 200 °C. The crystallinity index value increased from the initial 29.89% (untreated biomass) to 56.71% (120 °C treated) and 44.3% (140 °C treated), indicating that the hemicellulose started to hydrolyze under 120 °C, and parts of the cellulose began to hydrolyze with the rise of temperature. With the continuous increasing of reaction temperature, the crystallinity index decreased to 32.41% (160 °C treated) and 26.59% (200 °C treated). As with the XRD patterns, Fig. 9f shows the pure  $\alpha$ -cellulose after 200 °C treatment, in which most para-

crystalline regions and relatively amorphous regions were probably hydrolyzed, and the core part of crystalline structure remained. Figure 9 (a through e) shows the tendency of intensity to change with increasing temperature. This tendency was in agreement with SEM results, which demonstrated the gradual loss of hemicellulose and relatively amorphous cellulose with increasing temperature.



**Fig. 9.** XRD patterns of (a) untreated corn stover, (b) 120 °C treated corn stover, (c) 140 °C treated corn stover, (d) 160 °C treated corn stover, (e) 200 °C treated corn stover, and (f) 200 °C treated  $\alpha$ -crystalline cellulose

## CONCLUSIONS

1. This study provided insight into the conversion of hemicellulose and cellulose in a water/GVL system using different mineral acids as the catalyst. Sulfuric acid was a better candidate for LA generation, as it showed much higher selectivity in HMF conversion to LA than did hydrochloric acid.
2. High yields of furfural (75.12%) or LA (64.08%) were obtained individually in one-step hydrolysis; however, these high yields cannot be achieved at the same time due to the different optimal reaction conditions for furfural and LA. A two-step hydrolysis process was applied to optimize the conditions to achieve high yields of both furfural (70.65%) and LA (57.7%).
3. This two-step method can be used in a recycled hydrolysis process once the optimal conditions have been determined, and it shows excellent industrial potential as a method of utilizing biomass to generate high-value chemicals.

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