Influence of cellulose crystal plane on cellulose hydrolysis

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Abstract: Cellulose polymerization degree and crystal plane changing are both considered to affect acid hydrolysis, however, it is uncertain to identify which one is more important. In this study, the filter paper was treated with dilute hydrochloric acid to investigate the cellulose polymerization degree changing, and cotton linter was treated with NaOH for the purpose of changing its crystal plane. Both the treated and untreated samples were hydrolyzed under the condition of 1.0 wt% dilute hydrochloric acid with solid-liquid ratio 1:40 at 140°C for 30 min to compare the hydrolysis effects. It was found that the glucose yield increased from 9.5% to 19.7% when treated with 15% NaOH at 50°C for 30 min, and new crystal planes (1-10) (1-20) appeared after alkali treatment. According to the experimental results, it is concluded that crystal plane plays a vital role in cellulose acid hydrolysis.

Keywords: biomass, degree of polymerization, crystal plane, hydrolysis
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1 Introduction

During the last few decades, excessive consumption of fossil fuel has resulted in continuing environmental deterioration. Lignocellulosic biomass, mainly composed of cellulose, hemicellulose and lignin, is regarded as a promising alternative energy source due to its availability and renewability, and it has attracted extensive attention all around the world[1-4]. Agricultural residues are the most abundant lignocellulosic biomass resource in China. The monosaccharides can be obtained from the hydrolysis of lignocellulosic biomass. On this basis, a sugar platform can be established to produce a variety of liquid fuels or other high value-added chemicals[5,6]. This processing has been considered as a hopeful route to make up for the fossil fuels shortage. An efficient and economical hydrolysis processing becomes the key step of this route.

The hydrolysis of biomass can be classified into two types. One is acid hydrolysis (sulfuric acid and hydrochloric acid are most commonly used), and the other is enzyme hydrolysis. Both have been widely studied so far[7]. Effective enzymatic conversion of lignocellulose into fermentable sugars is difficult because of the sophisticated three-dimensional structure, which is composed of lignin, hemicellulose and cellulose[8]. In order to improve the efficiency of enzymatic hydrolysis, many studies on pretreatment including dilute acid[9], alkaline[10], ionic liquid[11,12], liquid hot water and ammonia pretreatments[13] have been presented over the years aiming to improve the enzymes accessibility to cellulose for the subsequent enzymatic hydrolysis. To date, the main challenges of enzymatic hydrolysis are the relatively high cost of enzyme production and pretreatment process.

There are some obvious disadvantages for processing

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with the dilute acid hydrolysis, such as poor sugar yields and relatively higher energy requirements[14,15], but it is characterized by a high hydrolysis rate, conversion degree and substrate adaptability. Some researchers have probed into the production of HMF and furfural by dehydration of saccharides using a biphasic reactor system[16,17] and some have explored the production of liquid alkanes[18].

Hemicellulose is relatively simple to be hydrolyzed using acids as catalyst[19-21]. However, cellulose is much tougher to be hydrolyzed to produce monosaccharides due to its high-ordered structure. Cellulose is a high molecular weight linear polymer composed of D-glucopyranose units linked by β-1, 4-glycosidic bonds[22]. The individual cellulose chains are joined by a network of inter- and intra-molecular hydrogen bonding which form the crystalline structure of cellulose. The cellulose crystalline regions alternate with amorphous regions[23-25]. So it is very difficult for cellulose to hydrolysis due to its perfect structure. However, the content of cellulose is the highest with approximately 40% followed by lignin and hemicelluloses. The processing of efficient hydrolysis cellulose to produce glucose has significant influence on the development of bioenergy products.

Degree of polymerization (DP), the number of glucose unit in a cellulose fibril, is believed to be a crucial feature for cellulose hydrolysis[26-28]. The average DP reflects the changes of cellulose during hydrolysis. The macroscopic variability regularity of DP had been extensively studied in the acid hydrolysis process of cellulose, and some results were obtained[29-31]. Apart from DP, the crystalline structure is another vital feature for cellulose hydrolysis. Cellulose I is the most abundant form found in nature. Cellulose II can be prepared by two distinct routes: mercerization (alkali treatment) and regeneration (solubilization and subsequent recrystallization). Celluloses III and IV can be obtained from celluloses I, II[32-34]. Considerable work has been done for the lignocellulosic fibers to ameliorate their crystal structures through mercerization process[35-39]. Cellulose is a substance with crystal structure, the cellulose hydrolysis reaction will occur on the crystal plane. The crystal plane of cellulose is one of the key influence factors which govern the acid hydrolysis. Few studies have been carried out on the effects of cellulose crystal plane change on cellulose acid hydrolysis.

In this study, the crystal plane will be changed using alkali treatment. The influence rule of crystal plane on cellulose dilute-acid hydrolysis will be investigated.

2 Material and methods

2.1 Raw material

In order to clearly investigate the effect of crystal plane on cellulose acid hydrolysis, Filter paper (FP, Whatman filter paper, DP=1088) and Dewaxed cotton linters (CL, DP=1087) were used as the cellulose materials in this study. Corn stover was collected from the north of Anhui province of China. High purity standard reagents for HPLC analysis were purchased from Sigma–Aldrich Chemicals. Hydrochloric acid (HCl, 36%-38%) and NaOH (purchased from Sinopharm Chemical Reagent Co., Ltd) were of reagent grade and were used without further purification.

2.2 Sample preparation

FP (cut into pieces) was mixed with hydrochloric acid of different concentrations (0.5 wt%, 1 wt%, 2 wt%, 3 wt%, 4 wt%, 5 wt%, 6 wt%, 7 wt%, 8 wt% and 9 wt%), temperatures (30°C, 40°C, 50°C, 60°C, 70°C, 80°C, 90°C, 100°C, 110°C and 120°C) and times (5 min, 10 min, 15 min, 20 min, 25 min, 30 min, 60 min, 90 min, 120 min and 150 min) in a 100 mL glass reactor equipped with magnetic stirring. The solid/liquid ratio was 1:40 for mixture. The samples' treatment proceeded in the glass reactor and then placed it into an oil bath to keep the target temperature. After reaction finished, cool the mixture with ice water. The solid phase was recovered by filtration with a vacuum pump and washed with a large amount of deionized water to remove excess acidity component. And then, the solid phase was freeze dried prior to characterization and the subsequent hydrolysis.

CL was mixed with NaOH solution (mass concentration 15%) in a 100 mL glass reactor under different temperatures (25°C and 50°C) and times (5 min and 30 min), with a solid/liquid ratio of 1:40. After the reaction, the prepared CL was cooled immediately by placing the glass reactor in ice slurry. After cooling down, the samples were filtered with a vacuum pump and washed with distilled water, neutralized with 2% acetic acid, finally washed again with distilled water until neutral and dried in the air for characterization and hydrolysis. Corn stover was also treated with 15% NaOH at 50°C for 30 min.

2.3 Acid hydrolysis

The materials (the original materials, prepared materials) were added to a 150 mL batch reactor with 1 wt% dilute hydrochloric acid. The solid/liquid ratio was 1:40. The hydrolysis experiment was carried out with vigorous stirring, the reaction time was 30 min and temperature was 140°C which needed approximately 35 min to reach. After the reaction, the reactor was removed from the heating jacket and cooled down with circulating water immediately. The hydrolysate was collected by filtration and an aliquot was used to analyze the concentrations of glucose and calculate the sugar yields.

2.4 Analysis methods

2.4.1 Sugar determination

The glucose in hydrolysate was determined using a high-performance liquid chromatography (HPLC) system. The HPLC system was equipped with SHODEX SP 0810 column (8×300 mm; Shodex, Tokyo) and differential refractive index detector (Waters 2414, USA). The temperatures of the column oven and detector were 85°C and 35°C, respectively. The mobile phase was deionized water with a flow rate of 0.6 mL/min. The yield of glucose was calculated using the following formula:

$$\text{Glucose yield} = (A\times 0.9)/B \quad (1)$$

where, A is glucose produced in the hydrolyzate, g; B is glucan in raw material, g.

2.4.2 Scanning electron microscopy (SEM)

SEM pictures of filter paper, cotton linter and treated filter paper, cotton linter were taken at a magnification of 500 times and 20 kV. All samples were sputter-coated with a thin layer of gold before taking pictures. Prior to determination, all wet samples were freeze dried to maintain their post-treatment structures and original samples were directly used for determination.

2.4.3 DP

The DP of cellulose was measured according to ASTM standard D1795[33]. A weighed sample of the material was dissolved in a 0.5M cupriethylenediamine hydroxide solution 40 min to make sure it was completely dissolved. The viscosity of this solution, and also that of the solvent, was determined at 25°C by means of a calibrated glass capillary-type viscometer. If both solution and solvent were measured in the same viscometer, the relative viscosity was calculated as follows:

$$\eta_{\text{rel}} = t / t_0 \quad (2)$$

where, η_{rel} is the relative viscosity; t is the outflow time of the solution; t_0 is the outflow time of the solvent. The intrinsic viscosity was calculated by interpolation using the USP table that lists the predetermined values of the product of intrinsic viscosity and concentration, then

$$\text{DP}^{0.905} = 0.75[\eta] \quad (3)$$

where, $[\eta]$ is the intrinsic viscosity.

2.4.4 Crystallinity index and indices of crystal plane

X-ray diffraction (XRD) was used to investigate the supermolecular structure of cellulose samples after different treatments. X-ray diffraction data were obtained using a Rigaku TTR-III X-ray instrument and the samples were planished. Ni-filtered Cu Kα radiation (λ=1.54 Å) generated at a voltage of 40 kV and current of 200 mA was utilized, and samples were scanned at a speed of 8 (°)/min, range from 2θ = 5° to 40°, and with a step size of 0.02° at room temperature.

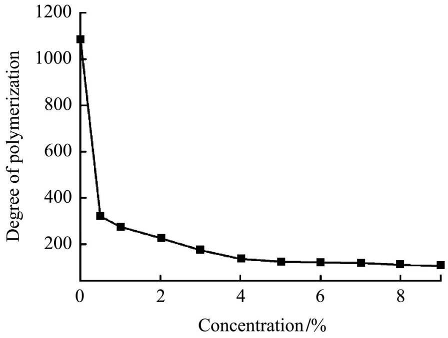
The crystal plane indices of all samples were also analyzed by using XRD technique combined with Rietveld refinement method.

3 Results and discussion

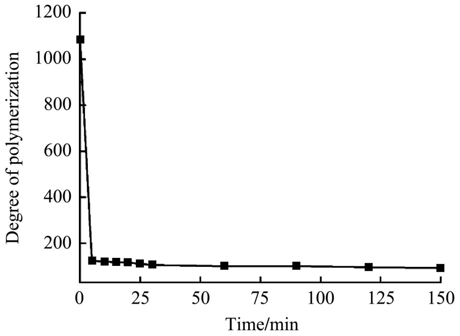
3.1 Effect of DP on cellulose dilute-acid hydrolysis to produce sugar

The value of initial DP (DP=1088) was taken when filter paper was left untreated. Different DPs of cellulose were prepared with hydrochloric acid under various conditions.

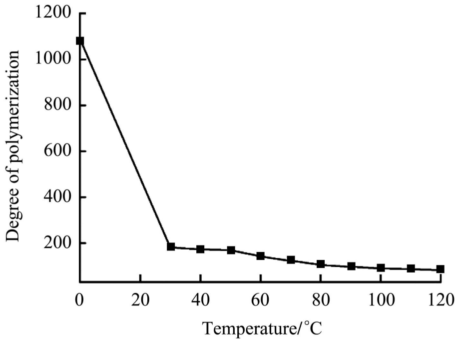
As shown in Figure 1, DP had a sharp decline in the initial phase. Figure 1a indicates the DP significantly decreased from 1088 to 320 as the hydrochloric acid concentration increased to 0.5%. Figure 1b shows the initial DP_0 of filter paper decreased rapidly from 1088 to 123 within the first 5 min. Figure 1c illustrates the effect of temperature on DP with 5% HCl for 5 min. DP quickly decreased to 181 from 1088 at 30°C. Then the DP underwent a slowly decrease as the reaction parameters (acid concentration, reaction time and reaction temperature) further improved. The decrease of DP was small compared with the initial stage. The DP curve remained relatively flat under harsh reaction conditions (acid concentration >5%, reaction time >5 min, reaction temperature>90°C). The effect of these three parameters (acid concentration, reaction time and reaction temperature) on final DP value was almost the same (around 105).



a. Concentration (5 min, 70°C)



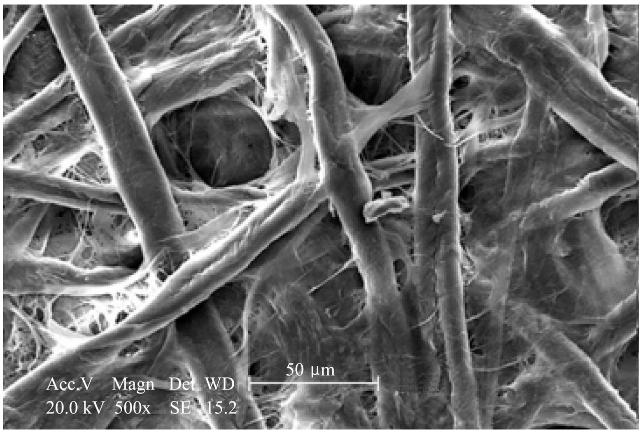
b. Time (5% HCl, 70°C)



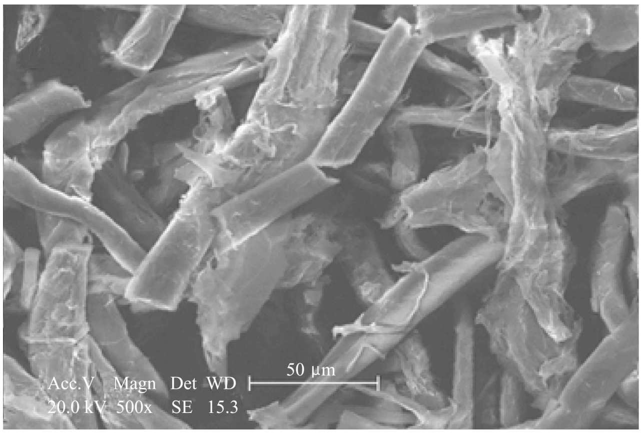
c. Temperature (5% HCl, 5 min)

Figure 1 Effect of hydrochloric acid on the DP of filter paper under different concentration, time and temperature

The experimental results as Figure 1 showed may be explained that the glycosidic linkages in the less ordered cellulose regions (amorphous) are easy to be cleaved in a random fashion, which can also be accounted for by SEM pictures (Figure 2). The surface of FP before acid treatment does not show the presence of any surface cracks or crushed fibers (Figure 2a). After acid treatment (Figure 2b), some large fissures could be clearly seen on the surface of the samples and the shortening of fibers occurred. These surface modifications have occurred as a result of the removal of amorphous regions from FP after acid treatment.



a. Untreated FP



b. Dilute hydrochloric acid treated FP (5% HCl, 70°C for 2.5 h)

Figure 2 SEM images of filter paper

As Table 1 showed, the DP value of filter paper was significantly reduced after acid treatment. With the DP decreasing from 1088 to 93 after acid treatment, the glucose yield was remarkably enhanced from 9.2% to 14.3%.

Table 1 Sugar yield of filter paper samples

Material	Treatment	DP	Sugar yield/%
Filter paper	Untreated	1088	9.2
	Treated[b]	93	14.3

Note: [b] dilute hydrochloric acid treated FP (5% HCl, 120 °C for 25 min).

Experimental data in Table 1 suggested a lower value of DP was corresponding to a higher sugar yield. From the above experiment results, a lower value of DP means the proportion of amorphous cellulose decreased and the crystalline cellulose proportion increased. The sugar yield of treated FP hydrolysis was higher than that of untreated FP. It is not consistent with the knowledge that the hydrolysis of crystalline cellulose is more difficult than that of amorphous cellulose. The so-called abnormal phenomenon may be explained by the X-ray diffraction patterns of FP samples before and after acid treatment (Figure 3).

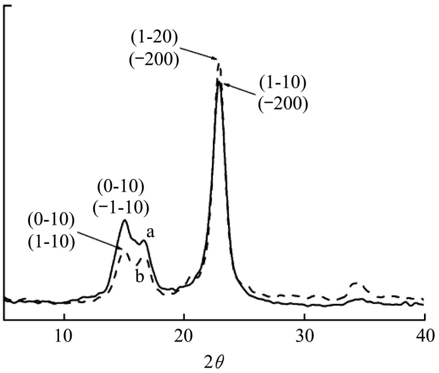


Figure 3 XRD patterns of (a) untreated FP and (b) dilute hydrochloric acid treated FP (5% HCl, 120°C for 25 min)

It could be found that the pattern of the FP exhibited a sharp high peak at 2θ=22.7° and a weaker diffraction peak at 2θ=15.2°. Pure cellulose exists in several crystalline polymorphs with different packing arrangements. The unit cells represent a quantity which mirrors these differences. During experimental data processing, the Bragg Equation ($n\lambda=2d\sin\theta$) was used to get d_{hkl} firstly, and then utilized the d_{hkl} under triclinic system to get the crystal indices according to Rietveld refinement method[35]. The crystal plane showed in Figure 3 was estimated in the P1 space group and triclinic crystal systems. The filter paper cellulose crystallized in a one-chain triclinic structure Iα and the data of unit cell was a=6.717Å, b=5.962Å, c=10.4Å, α=118.08°, β=114.8°, γ=80.37°. Each peak in the diagram was composed by several crystal faces.

In deep analyzing Figure 3, the crystal plane indices were changed a lot. The crystal plane changed from (1-10) (−200) to (1-20) (−200) at 2θ=22.7° and (0-10) (−1-10) to (0-10) (1-10) at 2θ=15.2° after treatment. So the anomaly experimental results that the decrease DP of filter paper followed by the increase of crystalline region contributed to higher hydrolysis efficiency may be explained as the effect of crystal plane.

3.2 Effect of crystal plane on cellulose hydrolysis to produce sugar

In order to further study how the crystal plane indices affected hydrolysis, dewaxed cotton linters were treated with NaOH in this part.

The cotton linters, before and after treatment with NaOH, were also hydrolyzed using 1 wt% dilute hydrochloric acid at 140°C for 30 min. The experimental results are showed in Table 2. The data suggested, after alkali treatment, though the DP was slightly changed, the sugar yield was remarkably enhanced from 9.5% to 19.7%.

Table 2 Sugar yield of cotton linters

Materials	Treatment	DP	Sugar yield
Cotton linters	Untreated	1087	9.5
	Treated[d]	996	15.2
	Treated[b]	985	18.3
	Treated[c]	973	19.7

Note: [d] NaOH treated CL (15% NaOH, 25°C for 5 min); [b] NaOH treated CL (15% NaOH, 25°C for 30 min); [c] NaOH treated CL (15% NaOH, 50°C for 30 min).

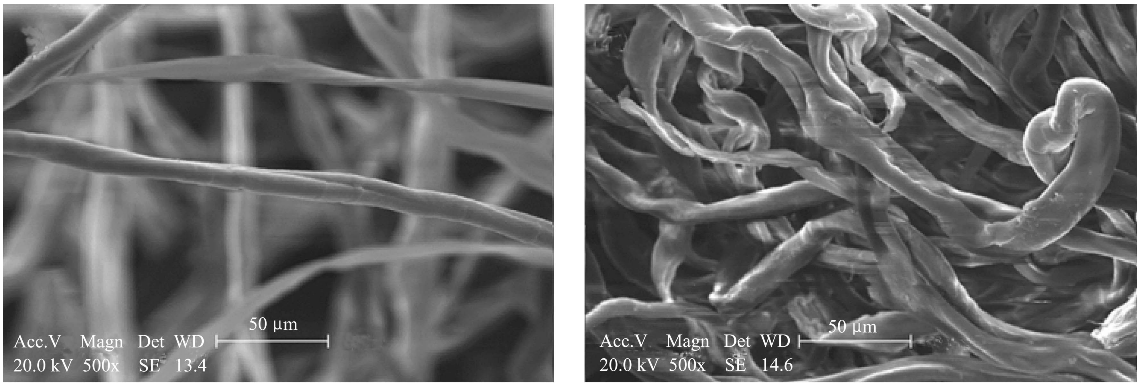
3.3 SEM of CL

The morphological structure of dewaxed cotton linters before and after NaOH treatment was observed using scanning electron microscopy. No cracks and shortening fibers treated with NaOH were observed in SEM pictures of cotton linters (Figures 4a and 4b). A phenomenon that fibrils became swollen was found after treatment. The phenomenon may be explained as follows, the dehydrated hydroxide ions penetrate the lattice at a certain alkali concentration and then the crystalline structure of the cellulose gets swelled and relaxed.

3.4 XRD of CL

The changes of cellulose crystal plane after alkali treatment under different conditions were investigated by Powder XRD, and the results were shown in Figure 5.

It was apparently that the crystal planes and the space groups were both changed a lot before and after 15% NaOH treatment under different time and temperature. The space group changed from P1 to P21. In the triclinic crystal system as Figure 5 showed, some crystal planes disappeared, such as the original (110) (2-11) crystal planes, and many new crystal planes formed, such as (0-20) (−11-2) (1-20). The two crystal planes (1-10) (1-20) appeared at 11.9° and 19.9° existed in all treated sample. When it was estimated in the monoclinic system, crystal plane changed from (1-10) (−1-12) to (0-1-2) (1-1-2) at 19.9°, (100) (0-10) to (0-1-1) at 11.9°.



a. Untreated CL

b. NaOH treated CL

Figure 4 SEM images of untreated CL and NaOH treated CL (16% NaOH, 25°C for 30 min)

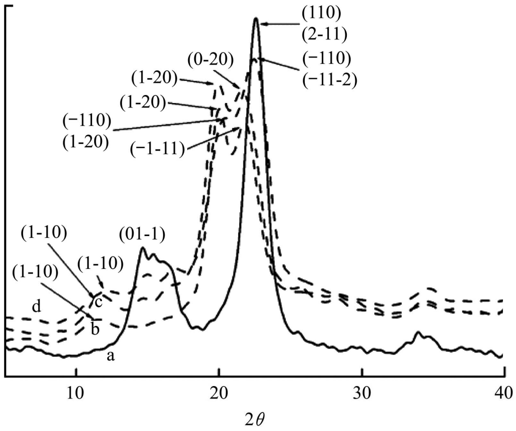


Figure 5 XRD patterns of (a) untreated CL, (b) NaOH treated CL (15% NaOH, 25°C for 30 min), (c) NaOH treated CL (15% NaOH, 50°C for 30 min) and (d) NaOH treated CL (15% NaOH, 25°C for 5 min)

NaOH treating on CL had slightly effect on its DP, while it resulted in the change of crystal structure, especially the crystal planes and the space groups. As the crystal planes changed, the hydrolysis efficiency improved significantly, leading to a dramatically glucose yield increase from 9.5% to 19.7%, which suggested that hydrolysis was closely related to the cellulose crystal plane. The hydrolysis reaction became much easier to occur on the newly formed crystal faces. Thus, crystal plane was considered an important factor on cellulose hydrolysis.

Corn stover was used as real biomass material to verify the experimental results, and it was also hydrolyzed using 1 wt% dilute hydrochloric acid at 140°C for 30 min. The results showed that the hydrolysis glucose yield of corn stover increased from 7.5% to 16.1% after alkali treatment (15%NaOH, 50°C, 30 min) following by the crystal planes changing.

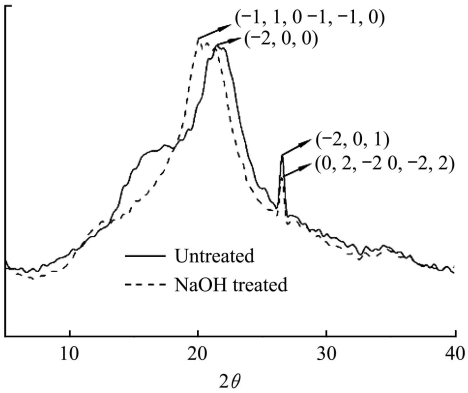


Figure 6 XRD patterns of untreated corn stover and NaOH treated corn stover

4 Conclusions

Cellulose crystal planes changed a lot after diluted hydrochloric acid or NaOH treatment. The crystal plane changed from (1-10) (−200) to (1-20) (−200) at 2θ=22.7° and (0-10) (−1-10) to (0-10) (1-10) at 2θ=15.2° after diluted hydrochloric acid treatment, and crystal plane changed from (1-10) (−1-12) to (0-1-2) (1-1-2) at 2θ=19.9°, (100) (0-10) to (0-1-1) at 2θ=11.9° after NaOH treatment. With the change of crystal plane in different crystal systems and space groups, the glucose yield increased from 9.5% to 19.7%, indicating that crystal plane is a key factor affecting cellulose hydrolysis. A similar rule is also suitable for corn stover, verifying crystal plane plays a more significant role on sugar yield.

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